REACTIONS OF (AZADIENE)TRICARBONYLIRON(0) COMPLEXES AND BROMINE INDUCED ALKENE/EPOXIDE INTERACTIONS

BY

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TABLE OF CONTENTS

DIELS-ALDER REACTIONS OF (1-AZADIENE)TRICARBONYLIRON(0) COMPLEXES

(2-AZADIENE)TRICARBONYLIRON(0) COMPLEXES

LIST OF TABLES

BROMINATION OF ALKENE/EPOXIDE MIXTURES

LIST OF DIAGRAMS

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DECLARATION

All the work described in this thesis, unless otherwise stated, was performed by the author in the Department of Chemistry, University of Warwick, between October 1987 and September 1990 and has not been previously submitted for a degree at any Institution.

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July 1991

SUMMARY

The bromination of alkene/epoxide mixtures leads to the formation of β,β'-dibromoethers ($BrCR_2CR_2OCR_2CR_2Br$) [R=H,Me] and dibromoalkanes. The amount of β,β'-dibromoether formed was optimised relative to the amount of dibromoalkane formed by carrying jout the reaction in pentane at -78 °C. The reaction is believed to proceed *via* a three step mechanism, two steps of which (the opening of bromonium ion by epoxide, and the opening of oxonium ion by Br^-) have been shown to occur stereospecifically.

(Cinnamaldehydeanil)/tricarbonyliron(0) (*4*), $(PhCHCHCHNPh)Fe(CO)_3$, a representative (1-azadiene)tricarbonyliron(0) complex can be prepared in 41% yield by heating cinnamaldehydeanil (*5*) (PhCHCHCHNPh) with $Fe_2(CO)_9$ (*17*). This yield could be improved to 82% by the use of ultrasound, or to 80% *via* a transfer reaction from a (1-oxadiene)tricarbonyliron(0) complex. 1-Azadiene complexes could themselves be used as a source of $-Fe(CO)_3$ for a transfer reaction to butadiene ligands, the first reported use of (azadiene)tricarbonyliron(0) complexes in this way. (1-Azadiene)tricarbonyliron(0) was found to be unreactive with respect to Diels-Alder reactions.

(2-Azadiene)tricarbonyliron(0) complexes (*109*) have never been reported. A series of 2-azadiene ligands ($ArCHNCHCHCH_3$) [Ar = Ph- (*114*); Ar = $4\text{-}ClC_6H_4$- (*116*); Ar = $4\text{-}MeOC_6H_4$- (*115*)] were prepared, but complexation with $Fe_2(CO)_9$ (*17*) or $Fe(CO)_5$ (*26*) did not produce a tricarbonyliron(0) complex. Complexation of (*115*) with $Fe_2(CO)_9$ (*17*), however, produced a $Fe_2(CO)_6$ containing compound (*118*) $[(4\text{-}MeO\text{-}C_6H_3\text{-}CH_2NCHCHCH_3)\text{-}Fe_2(CO)_6]$ in 10% yield.

ABBREVIATIONS

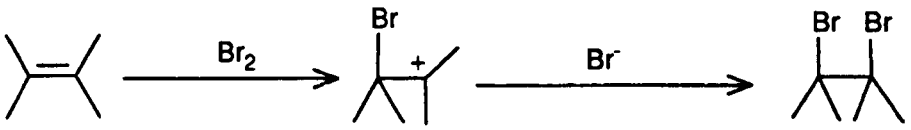
b.p.	boiling point
$b.p._{\cdot 758.4}$	boiling point at 758.4 mm Hg
C.I.	chemical ionisation
d	doublet
dd	doublet of doublets
ddt	doublet of doublet of triplets
dq	doublet of quartets
dec	decomposition
DMSO	dimethylsulphoxide
ee	enantiomeric excess
E.I.	electron ionisation
FAB	fast atom bombardment
hrs	hours
i.r.	infra red
lit.	literature
M^+	molecular ion
n.m.r.	nuclear magnetic resonance
q	quartet
r.t.	room temperature
s	singlet
THF	tetrahydrofuran
t.l.c.	thin layer chromatography
u.v.	ultra violet
v/v	volume by volume

BROMINATION OF ALKENE/EPOXIDE MIXTURES

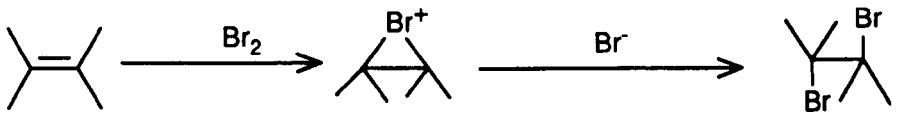
1. ADDITION REACTIONS TO ALKENE/EPOXIDE MIXTURES

1.1 The Formation and Nature of the Bromonium Ion.-

The bromination of simple alkenes is an electrophilic addition reaction, during which the formation of a cationic intermediate takes place. This intermediate could either be a carbocation (Scheme A), or a bridged bromonium ion (Scheme B).



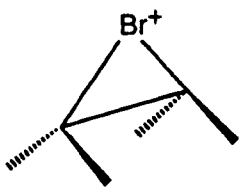
Scheme A



Scheme B

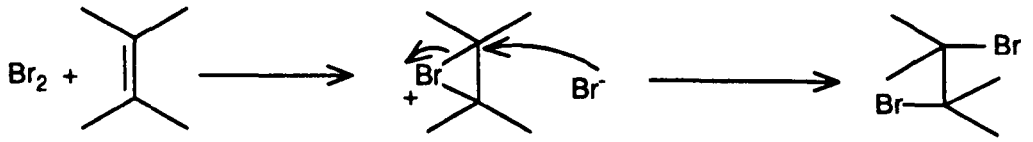
If the reaction proceeded *via* a carbocationic intermediate (Scheme A), free rotation about the carbon-carbocation bond would be possible. This would lead to a mixture of equal amounts of *syn*- and *anti*-brominated products.

In fact, for simple alkenes, only *anti*-brominated products are obtained, which suggests that there is restricted rotation about the carbon-carbon bond. A cyclic intermediate, as in Scheme B, would have the necessary restricted rotation to produce only *anti*-brominated products. The bromonium ion (I), where bromine uses one of its unshared electron pairs to bond with both carbons of the double bond was, therefore, proposed as the cationic intermediate in bromination reactions[1].



(I)

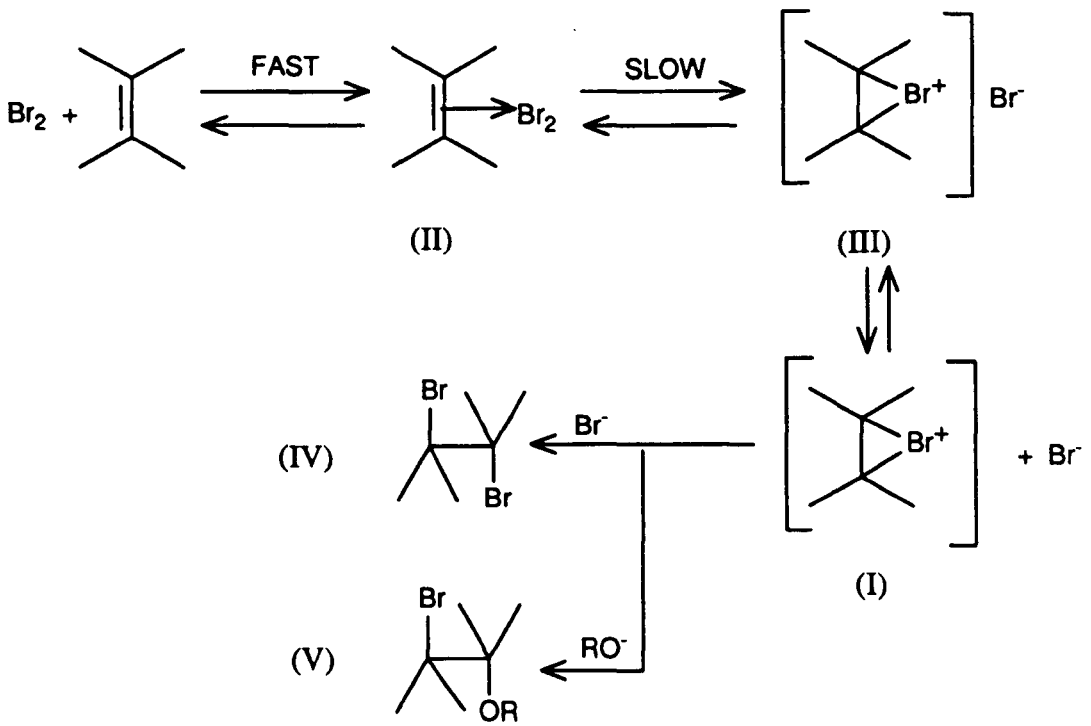
The bromide ion (Br^-) subsequently has to attack from the underside of the intermediate to give *anti*-addition as represented below:



(I)

1.1.1 Intermediates in bromination.

The following mechanism for the bromination of simple alkenes has been proposed[2]:



Initially a bromine molecule and the alkene interact to form a π-complex (II). π-Complexes of this type have been isolated and their structure confirmed spectroscopically[2,3]. The π-complex (II) is then slowly converted into an 'ion-pair' (III). In solvents with a high solvating capacity the ion-pair (III) dissociates into two solvated ions - bromonium ion (I) and anion Br^-. In non-polar, weakly solvating media this

intermediate is a solvent-separated pair[4], closer in structure to (III).

Evidence for the π-complex nature of transition states in bromination reactions was provided by rate studies on the bromination of simple alkanes in the non-polar solvent 1,1,2-trichlorotrifluoroethane[5].

The rate determining step for the reaction is the formation of the ion-pair (III) by the ionisation of π-complex (II). The dissociation of complex (II) is assisted by the solvent in protic media, and by a second bromine molecule in non-protic media[6]. Once the bromonium ion (I) is formed two products are possible:

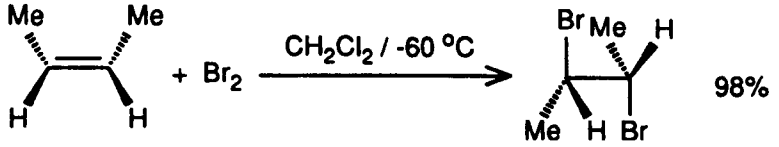
(i) dibromide (IV) by reaction of bromonium ion (I) with bromide ion, or

(ii) bromoether (V) by reaction with another available nucleophile (*e.g.* solvent).

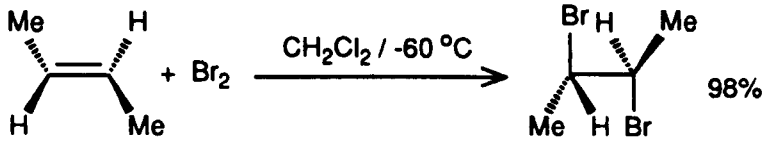
These products are formed rapidly and simultaneously. Depending on specific conditions (*e.g.* solvent polarity, structure of reagents, and reaction temperature) the precise details of this mechanism will vary and must be modified accordingly.

Apart from deductions based on the stereochemistry of the additions, direct evidence for the existence of cyclic intermediates such as (I) is difficult to obtain. Rate data on the bromination of substituted alkenes, however, has shown the charge distribution in the later transition states of bromination to be symmetrical, and this does imply bromine bridging in the intermediate[7]. The existence of these intermediates is supported by spectroscopic studies and theoretical calculations[6].

The mass of evidence suggests that simple ethylene derivatives undergo addition of bromine by the formation of a cyclic bromonium ion (I). This approach can be used to explain product formation in a large number of reactions, *e.g.* the bromination of *cis*- and *trans*-but-2-ene, (VI) and (VII) results in completely stereospecific *anti*-addition. No *syn*-addition, resulting from free rotation, is observed[8].



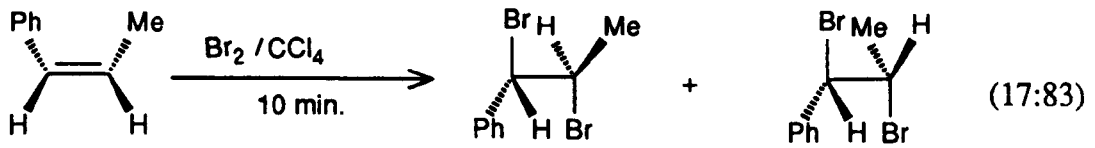
(VI)



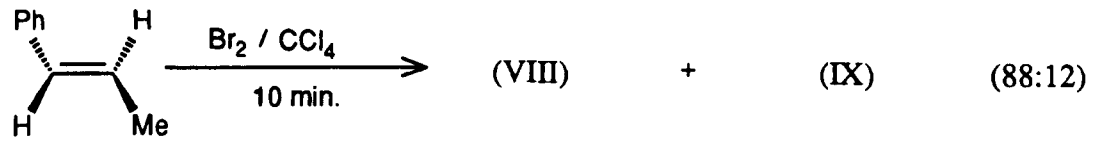
(VII)

1.1.2 Evidence for other mechanisms.

Evidence for carbocationic intermediates has, however, been obtained from some substrates, *e.g.* the bromination of both *cis*- and *trans*-1-phenylpropene (Scheme C) gave a mixture of *syn*- and *anti*-addition products [(VIII) and (IX)]. *anti*-Addition still predominated but it was not exclusive[9].



(VIII) (IX)



Scheme C

Bromination *via* a bromonium ion (I) should furnish only one isomer in each case.

The presence of substituents capable of stabilizing a positive charge on the carbocation was found to decrease the amount of *anti*-addition, *i.e.* to increase the carbocationic nature of the intermediates at the expense of the bromonium ion (see Table 1 overleaf).

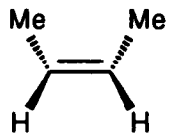
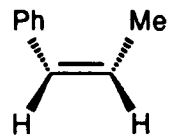
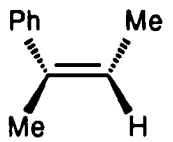
Alkene	% *anti*-addition
 (VI)	100
	73
	63

Table 1: Percentage *anti*-addition in the bromination of some alkenes[8]

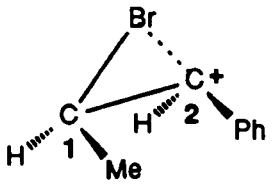
The stereochemistry of bromination also depends on solvent. *Cis*- and *trans*-but-2-ene, (VI) and (VII), which react only *via* a bromonium ion, give 100% *anti*-addition in all solvents. *Anti*-addition to *cis*-1-phenylpropene, however, decreases as the dielectric constant of the medium increases (see Table 2).

Solvent	Dielectric Constant	% *anti*-Addition
CH_3CO_2H	6.6	73
CH_2Cl_2	9.1	70
Ac_2O	21	49
C_6H_5-NO_2	35	45

Table 2: Bromination of *cis*-1-phenylpropene[10]

The alteration in stereochemistry appears to be due to the formation of a carbocationic

intermediate (X) which has a weak ionic bridge between the cation and the bromine atom in solvents of low dielectric constant, giving intermediate (X) some bromonium ion character.



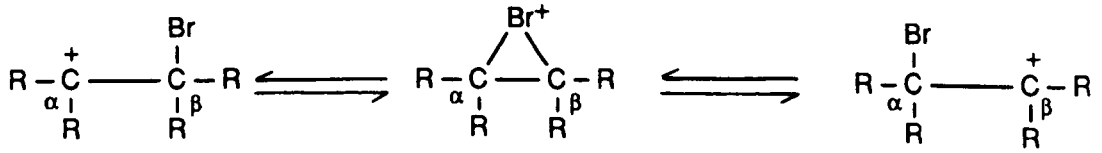
(X)

Substituents which stabilize the positive charge, or solvents which will solve the cation more efficiently will increase the carbocationic character of the intermediate, and allow rotation of the carbon$_1$-carbon$_2$ bond leading to both *syn*- and *anti*- products.

It thus appears, that there is a range of possible intermediates from bromonium ions to carbocations encompassing intermediates with more or less character from each system[11].

1.1.3 Additions to intermediates.

If the bromination reaction is carried out in a nucleophilic solvent, the solvent itself can attack the bromonium ion to lead to solvent-incorporated products. Regioselectivity will depend upon the relative charges borne by the two carbon atoms of the intermediate[12], as represented below:



For carbocations, solvent incorporation must be 100% regioselective because one carbon atom bears all the positive charge. For bromonium ions the charge distribution is less straightforward. On the whole, nucleophile additions follow Markovnikov's rule[6].

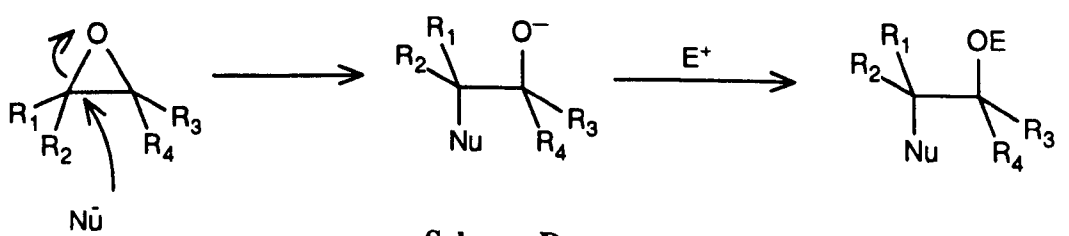
Chemoselectivity between two nucleophiles, usually the bromide ion and a nucleophilic solvent, depends on their relative nucleophilicities and on the electrophilicity of the intermediate. Detailed studies have been carried out only on the competition between Br^- and CH_3CO_2H[8] or MeOH[12]. Generally, MeOH appears to compete with Br^- better than CH_3CO_2H. Empirically, there seems to be more solvent incorporation when carbocations are intermediates than when bromonium ions are intermediates.

1.1.4 Summary of alkene bromination.

The intermediate structures in bromine addition, and, therefore, the product selectivities, are governed by the substitution on the alkene. When none of the substituents can stabilize the generated positive charge better than the bromine atom the intermediate is a bromonium ion and addition is 100% stereoselective. Regio- and chemoselectivities are difficult to predict. When very stable carbocations can be formed (*e.g.* with aryl or electron-donating substituents) then the intermediate has little or no bromonium ion character. Addition will be highly regio- and chemoselective but nonstereoselective[6].

1.2 Nucleophilic Attack On Epoxides.-

Epoxides bear some structural resemblance to the cyclic bromonium ion (I). Epoxides, like bromonium ions, are attacked by nucleophiles at one of the ring carbon atoms. The rings open to leave a free oxide function available for further reaction with electrophiles (see Scheme D):

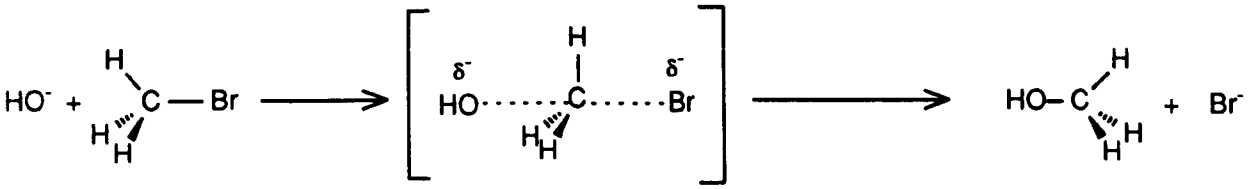


Scheme D

1.2.1 Regiochemistry of nucleophilic attack.

The regiochemistry of the attack of nucleophiles on epoxide ring systems can be explained by reference to the transition state for the reaction[13].

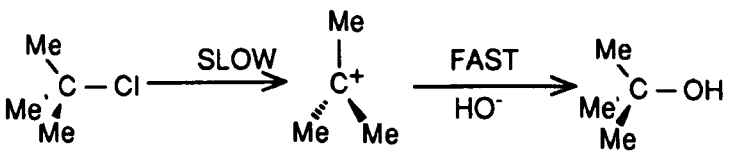
A typical nucleophilic substitution reaction, proceeding *via* an 'S_N2' pathway, involves a transition state such as (XI) in the hydrolysis of methyl bromide (XII)



(XII) (XI)

The negative charge in transition state (XI) is spread from the approaching OH^- ion, through the central carbon atom, to the departing Br^- ion. The reaction is one-step with no intermediate and the carbon-oxygen bond is formed as the carbon-bromine bond is broken. The attacking nucleophile (OH^-) attacks from a position 180 ° away from the leaving group and there is inversion of the configuration at the carbon atom[14].

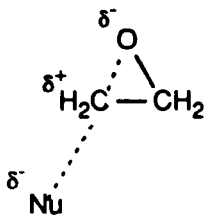
A reaction proceeding *via* an 'S_N1' pathway, passes through an intermediate such as (XIII) in the hydrolysis of *t*-butylchloride (XIV).



(XIV) (XIII)

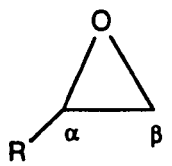
This is a two-step reaction. The first step is a slow ionization of the substrate to form an ionic intermediate rather than a transition state, with a formal positive charge. This is followed by rapid addition of the nucleophile[14].

Epoxide opening proceeds *via* a 'borderline S_N2' pathway[13]. The mechanism is essentially S_N2 but the transition state (XV) has some S_N1 character *i.e.* there is some charge distribution between the carbon and oxygen atoms because the carbon-oxygen bond breaks before the carbon-nucleophile bond forms.



(XV)

This transition state model has been used to explain the regiochemistry of nucleophilic attack in acidic and non-acidic media.



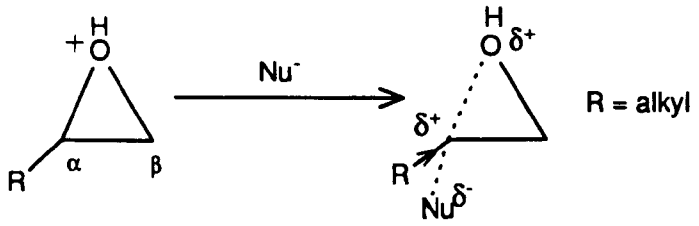
Substituent - R	Position of Attack	
	Acidic Media	Non-Acidic Media
alkyl	α or β	β
electronegative/non-conjugating	β	β
π-conjugating	α or β	α or β
n-conjugating	α	α

Table 3: Position of nucleophilic attack on substituted expoxides[13]

a) alkyl substituents

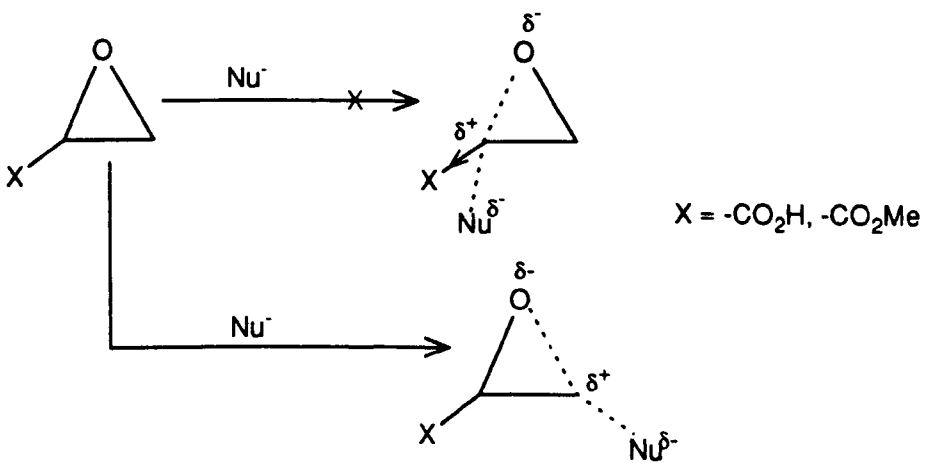
In non-acidic media, the steric bulk of the alkyl group blocks the nucleophile and it attacks only at the β-carbon.

In acidic media, electronic effects become important. The transition state has relatively more S_N1 character because the epoxide is protonated (see diagram below). The α-carbon is better able to stabilize a positive charge than the β-carbon because of the inductive effect of the alkyl group and addition is promoted, therefore, at the α-carbon. Steric factors may still, however, be sufficiently great to induce some attack at the β-carbon.



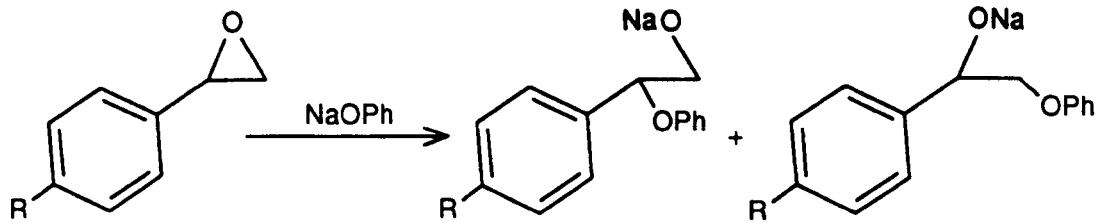
b) electronegative and non-conjugating substituents

These groups will interact with the transition state only *via* their inductive effect. They will destabilize a positive charge formed at the α-carbon and, therefore, reduce attack at the α-carbon atom (see below):



c) π-conjugating substituents

A good π-donor substituent stabilizes a positive charge at the α-carbon and addition occurs exclusively at the α-carbon. Less good π-donors, however, will produce a mixture of addition at the α- and β-carbon atoms because the steric effects of the substituent itself and of the nucleophile become relatively more important. The trend can be illustrated by nucleophilic attack on substituted styrene oxides (XVI)[15].



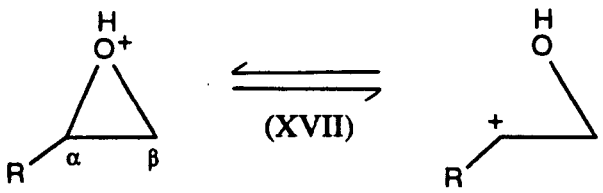
(XVI)

	% C_α addition	% C_β addition
$R = NO_2$	36	64
R = H	76	24
R = OMe	100	0

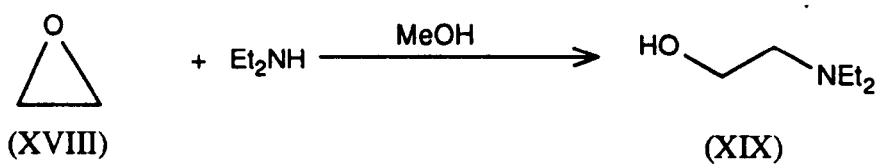
As the +R effect of the substituent increases the proportion of addition at the α-carbon increases as well.

d) n-conjugating substituents

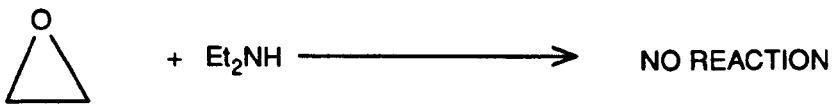
These groups stabilize a positive charge at the α-carbon very well and addition is at the α-carbon in almost all cases. The addition of nucleophiles is often accelerted in acidic media because of the formation of the more reactive conjugate acid (XVII) of the epoxide[15].



The transition states for these reactions all have at least some ionic character and nucleophilic attack can be accelerated, therefore, if it is carried out in polar solvents, *e.g.* the opening of ethylene oxide (XVIII) by diethylamine proceeds readily in methanol to give (XIX) but does not occur at all in the absence of polar solvents[15].



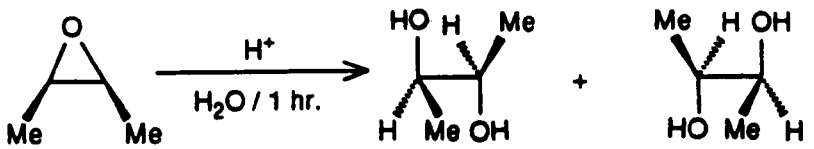
(XVIII) (XIX)



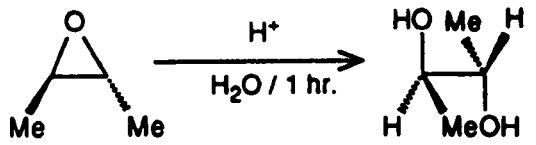
(XVIII)

1.2.2 Stereochemistry of nucleophilic attack.

The attack of a nucleophile on the carbon atom of an epoxide ring usually results in inversion of the configuration of substituents at that carbon atom, as would be expected for an essentially S_N2 reaction. For example, the opening of *cis*-2,3-epoxybutane (XX) and *trans*-2,3-epoxybutane (XXI) gave different products, inversion taking place at the carbon atom attacked by the nucleophile in each case[16].



(XX)

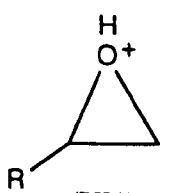


(XXI)

There are a few examples where epoxides open with retention and not inversion of configuration[17]. These usually occur when very good π- or *n*-electron-donating substituents are present which stabilize the positive charge on the α-carbon so well that the reaction becomes essentially 'S_N1'. Retention of configuration will then become more probable and there is a direct relationship between the ability of a substituent to stabilize a cationic centre at the time of carbon-oxygen bond cleavage and the proportion of retention, rather than inversion, at the α-carbon during ring opening[18].

1.3 Electrophilic Attack on Epoxides.-

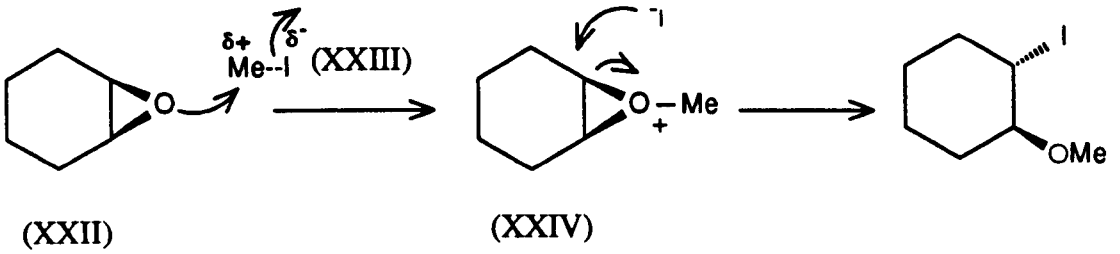
The oxygen atom of an epoxide ring contains two lone pairs of electrons which are available for reaction with electrophilic reagents. For example, epoxides react with proton donors to form conjugate acids such as the cyclic oxonium ion (XVII).



(XVII)

Usually, electrophilic attack on the oxygen atom of an epoxide is followed by nucleophilic attack at a carbon atom to open the ring[19] (as in Section 1.2). The reaction between the

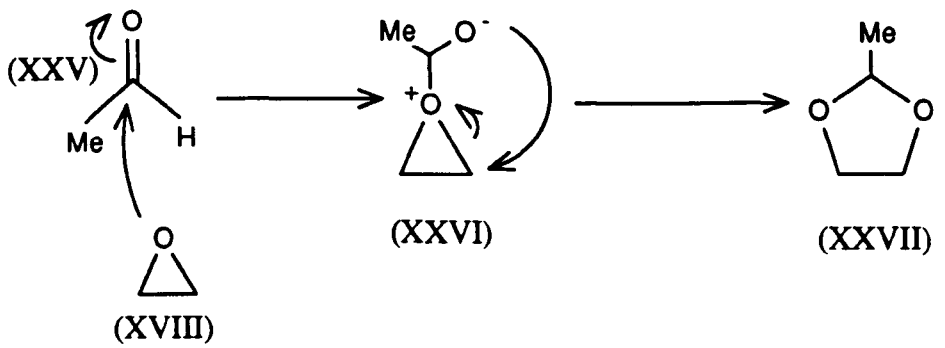
epoxide cyclohexene oxide (XXII) and the electrophilic alkyl halide methyl iodide (XXIII) (Scheme E) proceeds *via* electrophilic attack on the epoxide oxonium ion (XXIV). This oxonium ion (XXIV) is then opened by nucleophilic attack at a ring carbon atom by the liberated iodide ion (I^-)[19].



(XXII) (XXIV)

Scheme E

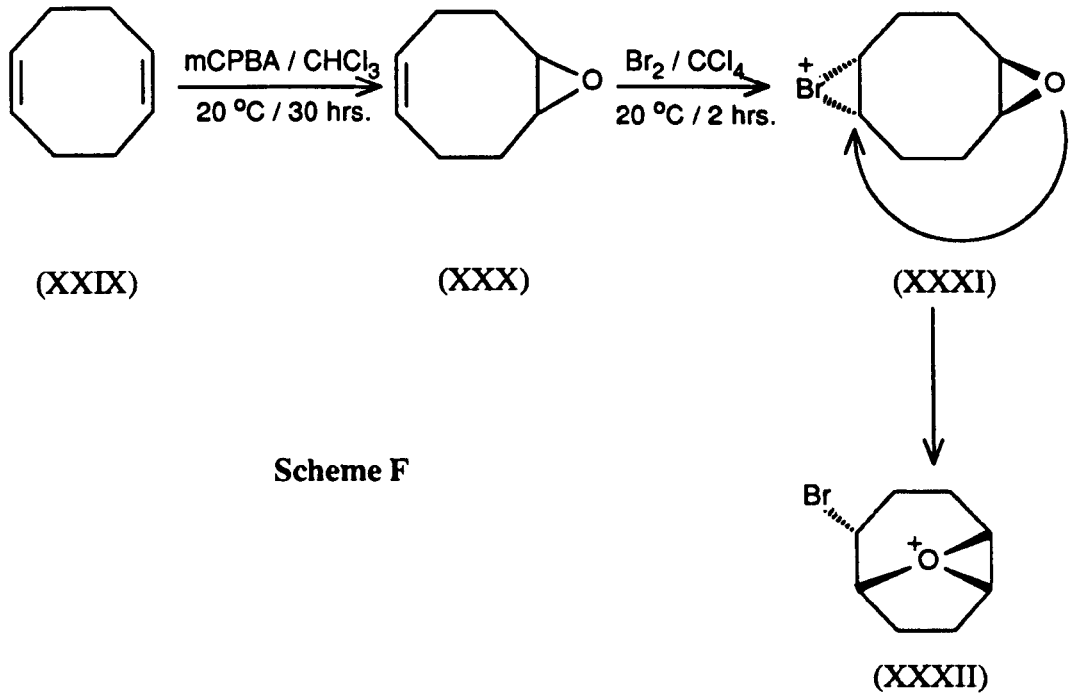
Other electrophilic reagents, such as carbonyl compounds, react wth epoxides in a similar manner. For instance, ethanal (XXV) reacts with ethylene oxide (XXIII) to form the cyclic oxonium ion (XXVI), which on this occasion is opened *via* an intramolecular nucleophilic attack to leave a five-membered heterocycle (XXVII)[20].



(XVIII) (XXVI) (XXVII)

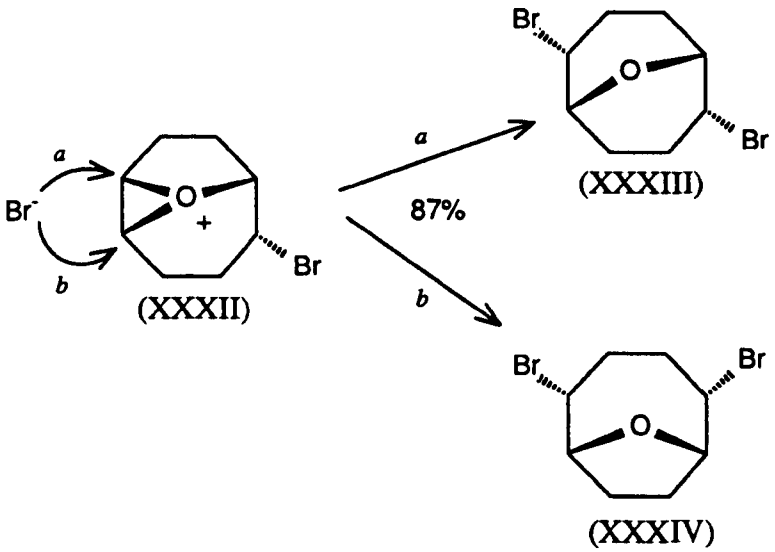
1.4 The Interaction of Bromonium Ions with Epoxides.-

If a bromonium ion is generated in the presence of an epoxide then an interaction between them may occur.

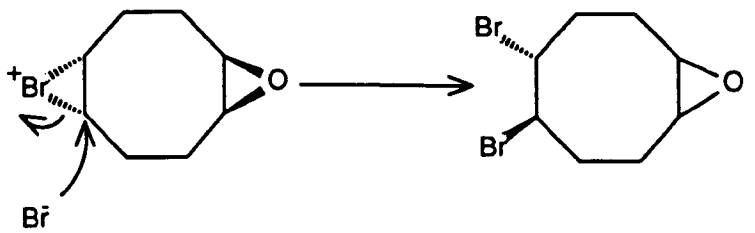


Scheme F

The treatment of unconjugated cyclic diene (XXIX) with one mole-equivalent of *m*-chloroperbenzoic acid (mCPBA) results in the formation of epoxidized alkene (XXX) (Scheme F)[21]. If this alkene (XXX) is allowed to react with a solution of bromine, intermediate (XXXI) is formed which contains both a cyclic bromonium ion and the epoxide functionality. Nucleophilic attack of the epoxide on the bromonium ion then occurs readily to form a tricyclic oxonium ion (XXXII). Subsequent nucleophilic attack by bromide ion on the oxonium ion (XXXII) then takes place *via* two alternative pathways (*a* or *b*) to generate two different cyclic ethers (XXXIII) and (XXXIV) in a ratio of 1.2:1.



The attack of the epoxide on the bromonium ion (XXXI) might be expected to compete with opening of the bromonium ion by the liberated bromide ion (Scheme G).

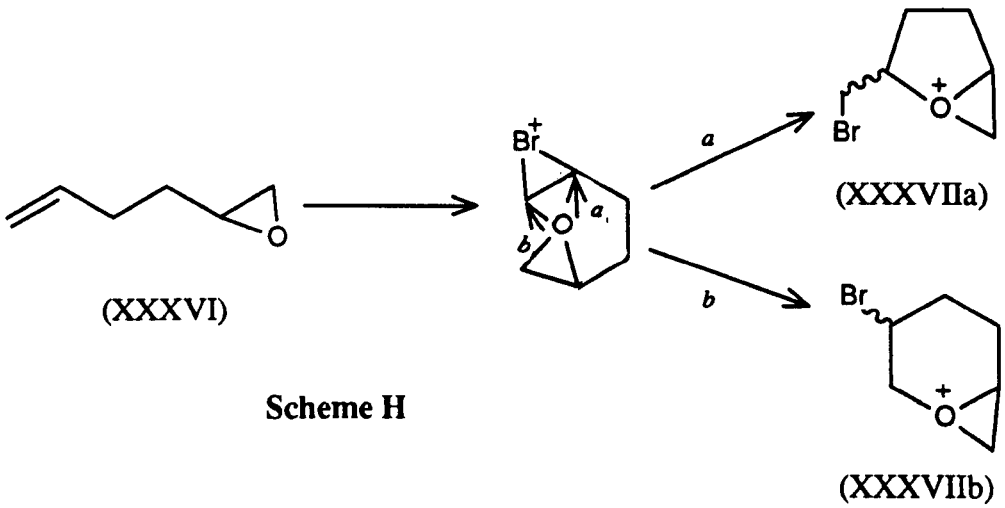


(XXXI) (XXXV)

Scheme G

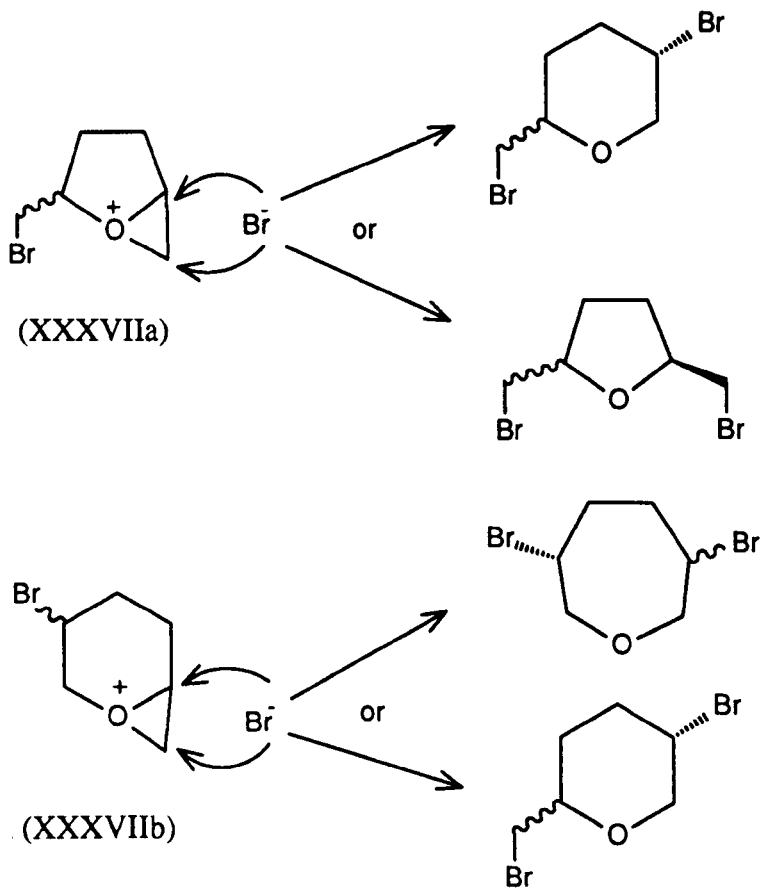
No trace of dibromide (XXXV), however, could be detected.

Cyclo-octane rings readily undergo interannular interactions. The conformational properties of the cyclo-octane ring, however, were found not to be essential for this reaction to occur. Bromination of 1,2-epoxyhex-5-ene (XXXVI) also resulted in nucleophilic attack of an epoxide on a cyclic bromonium ion (Scheme H)[21].

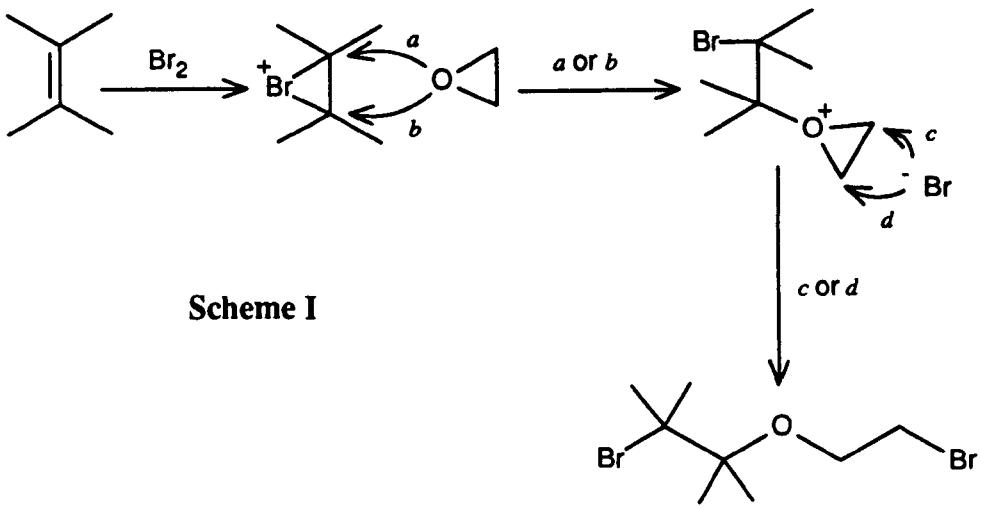


Scheme H

This attack may also open the bromonium ion by either of two pathways (*a* or *b*) to give a five- or six-membered cyclic oxonium ion (XXXVIIa) and (XXXVIIb) respectively. Both oxonium ions may be opened *via* nucleophilic attack by bromide ion to leave a range of products.

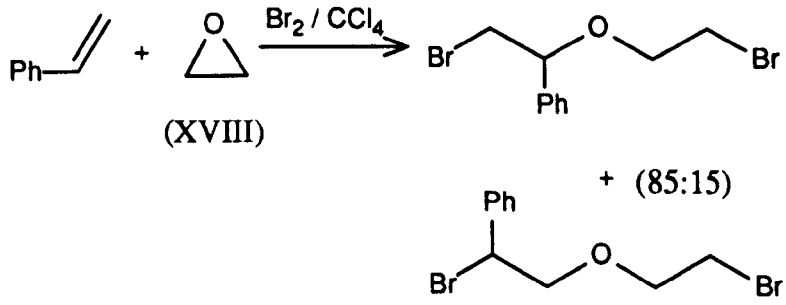


Both functionalities do not have to be present in the same molecule in order for the interaction between bromonium ions and epoxides to occur. The intermolecular reaction is predicted to proceed *via* a related pathway (Scheme I).



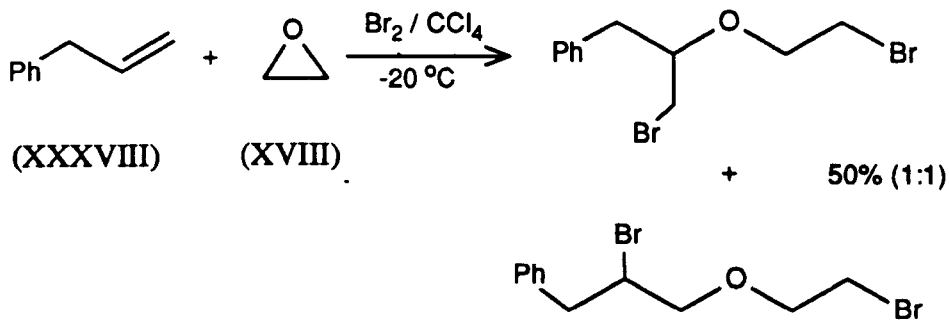
Scheme I

This intermolecular version of the reaction has been reported. For example, addition of bromine to styrene/ethylene oxide (XVIII) mixtures produces a mixture of dibromoethers[27].



(XVIII)

Similarly, the bromination of a mixture of allylbenzene (XXXVIII) and ethylene oxide (XVIII) also gives a mixture of dibromoethers[23].



(XXXVIII) (XVIII)

The majority of intermolecular halogen additions to alkene/epoxide mixtures reported previously have been performed without solvent[24,25] or in chloroalkane solvents. Most reactions were also carried out at temperatures close to room temperature. As far as we are aware, there has not been any systematic study of

a) the effect of temperature and solvent on this reaction, and

b) the stereochemical outcome of the reaction.

2. STEREOCHEMICAL CONSEQUENCES OF THE BROMINATION OF ALKENE/EPOXIDE MIXTURES

A systematic study of the bromination of alkene/expoxide mixtures has not appeared in the literature. In particular, the stereochemical consequences of the reaction have not been reported. In view of the potential applications of the dibromoethers formed (especially those which contain an array of chiral centres) to, for example, crown ether chemistry or transition-metal ligand chemistry, it was decided to study systematically the bromination of alkene/epoxide mixtures.

2.1 Bromination of 2,3-Dimethylbut-2-ene (XXXIX)/Ethylene Oxide (XVIII) Mixtures.-

The first experiments performed were designed to optimise the reaction conditions. The bromination of 2,3-dimethylbut-2-ene (XXXIX) and ethylene oxide (XVIII) was chosen for this investigation because

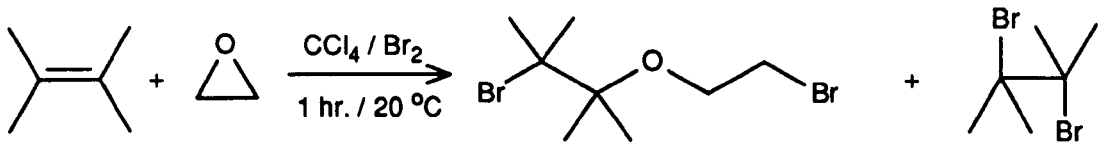
a) the high degree of symmetry of the two organic molecules means that there are neither regiochemical nor stereochemical complications,

b) the alkene and epoxide are both commercially available and relatively easy to handle, and

c) the simplicity of the ^1H n.m.r. spectrum of the product mixture should facilitate rapid analysis.

A solution of ethylene oxide (XVIII) in carbon tetrachloride was prepared by condensing ethylene oxide (XVIII) into a cooled measuring cylinder sealed with a rubber septum and diluting it with carbon tetrachloride. An aliquot containing a known amount of ethylene oxide (XVIII) was removed, diluted with more carbon tetrachloride and stirred at room temperature. One mole-equivalent of 2,3-dimethylbut-2-ene (XXXIX) was added. A carbon tetrachloride solution containing 1.3 mole-equivalents of bromine was then added to the stirred reaction mixture portionwise over 1 hour. The resulting orange solution was

washed with sodium thiosulphate solution and then with water. Drying over magnesium sulphate, filtration, and then concentration *in vacuo* left a white gum. The 220 MHz ^{1}H n.m.r. spectrum of this material contained two six-proton singlets at δ 1.40 [$(C\underline{H}_3)_2CO$], and δ 1.84 [$(C\underline{H}_3)_2CBr$], and two two-proton triplets at δ 3.45 (*J* 6 Hz, -$C\underline{H}_2O$-) and δ 3.75 (*J* 6 Hz, -$C\underline{H}_2Br$), all arising from the dibromoether (XL). The spectrum also contained a singlet at δ 2.05 due to the methyl protons of dibromide (IV). The ratios of the integrals of the methyl resonances in the ^{1}H n.m.r. spectrum revealed that the product mixture contained 26% dibromoether (XL) and 74% dibromide (IV).



(XXXIX) (XVIII) (XL) (IV)

(26:74)

Thus, the conditions described above favour the attack of bromide ion on the bromonium ion formed by addition of bromine to alkene (XXXIX) over the attack of epoxide. Experiments were performed, therefore, to increase the relative proportion of dibromoether obtained from the reaction.

The experiment described above was repeated using either two- or three-mole equivalents of ethylene oxide (XVIII). The results of these experiments are shown in Table 4:

No of equivalents of epoxide (XVIII)	Ratio of dibromoether (XL): dibromide (IV) (by ^{1}H n.m.r. spectroscopy)
1	26 : 74
2	34 : 66
3	48 : 52

Table 4: Ratio of dibromoether (XL): dibromide (IV) from the bromination of 2,3-dimethylbut-2-ene (XXXIX)/ethylene oxide (XVIII) mixtures

Thus, the relative proportion of dibromoether (XL) formed was found to increase as the amount of epoxide used was increased.

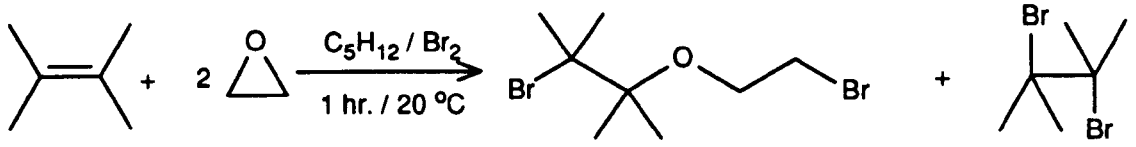
It was decided to use two mole-equivalents of epoxide in subsequent reactions since this provided a reasonable yield of dibromoether without being too wasteful of the epoxide component. (Although ethylene oxide is readily available, some of the epoxides used in later experiments are more valuable).

The effect of the solvent used in the reaction was then investigated. A solution of ethylene oxide (XVIII) was prepared in a range of different solvents. An aliquot of the solution was diluted with the same solvent and stirred with 0.5 mole-equivalents of 2,3-dimethylbut-2-ene (XXXIX). Treatment with a solution of bromine in the appropriate solvent over 1 hour and work-up as before, gave a series of white gums which were analysed by 220 MHz ^{1}H n.m.r. spectroscopy. The results are summarised in Table 5.

Solvent	Dielectric constant	Ratio of dibromoether (XL): dibromide (IV) (by ^{1}H n.m.r. spectroscopy)
CH_2Cl_2	9.08	16 : 84
$CHCl_3$	4.81	27 : 73
CCl_4	2.24	34 : 66
C_5H_{12}	1.84	37 : 63

Table 5: Ratio of dibromoether (XL): dibromide (IV) formed in the bromination of 2,3-dimethylbut-2-ene (XXXIX)/ethylene oxide (XVIII) mixtures in different solvents

The results in Table 5 reveal that the formation of dibromoether (XL) is favoured over formation of dibromide (IV) by decreasing the polarity of the solvent used. It was decided, therefore, to carry out future reactions in pentane to maximize the yield of dibromoether (XL) obtained.



(XXXIX) (XVIII) (XL) (IV)

(37:63)

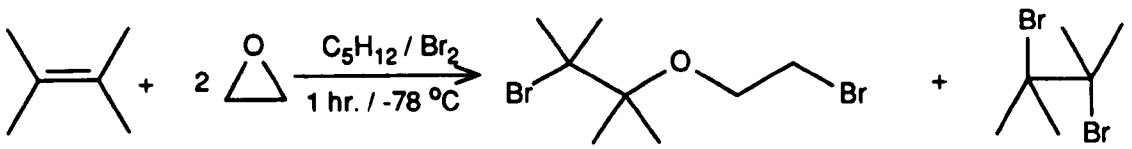
The effect of reaction temperature was then examined. The bromination of 2,3-dimethylbut-2-ene (XXXIX) with 2 mole-equivalents of ethylene oxide (XVIII) in pentane was performed over a range of temperatures. Work-up as before again gave a range of white gums which were analysed by 220 MHz ^{1}H n.m.r. spectroscopy. The results are summarised in Table 6.

Temperature (°C)	Ratio of dibromoether (XL) : dibromide (IV) (by ^{1}H n.m.r. spectroscopy)
20	37 : 63
-23	54 : 46
-78	67 : 33

Table 6: Ratio of dibromoether (XL): dibromide (IV) formed in the bromination of 2,3-dimethylbut-2-ene (XXXIX)/ethylene oxide (XVIII) mixtures at different temperatures

It may be seen from the results presented in Table 6 that decreasing the reaction temperature favours the formation of dibromoether (XL) over the formation of dibromide (IV).

Thus the optimum conditions obtained for the bromination of a mixture of 2,3-dimethylbut-2-ene (XXXIX)/ethylene oxide (XVIII) are using 2 mole-equivalents of epoxide in pentane at a temperature of -78 °C.



(XXXIX) (XVIII) (XL) (IV)

(67:33)

Chromatography of the crude reaction mixture, followed by distillation *in vacuo*, led to the isolation of the previously unreported dibromoether (XL) as a clear, colourless liquid, $b.p._{758.4}$, 175-178 °C in 38% yield.

The ^{13}C n.m.r. spectrum was assigned, with the aid of additivity rules, as follows: δ 21.6 (-OC($\underline{C}H_3)_2$-), 29.9 (BrC($\underline{C}H_3)_2$-), 31.1 (Br$\underline{C}H_2$-), 63.3 (-O-$\underline{C}H_2$-CH_2Br), 73.1

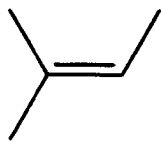
($BrC(CH_3)_2$-), and 79.9 ($-OC(CH_3)_2$-). The ^1H n.m.r. spectrum was assigned by comparison with values for alkyl bromides and alkyl ethers as follows: two six-proton singlets at δ 1.38 ($-C(CH_3)_2O$-) and δ 1.78 ($BrC(CH_3)_2$-), and two two-proton triplets at δ 3.38 (*J* 6.2 Hz, $-OCH_2$) and δ 3.71 (*J* 6.2 Hz, $BrCH_2$-). The mass spectrum (C.I.) contained an $[M + NH_4]^+$ peak with the expected 1:2:1 isotope pattern for a compound containing 2 x Br (308, 12%; 306, 28%; 304, 13%) and a base peak (165, 73%; and 163, 100%) corresponding to $[((CH_3)_2C)_2Br^+]$. Bromoether (XL) gave a satisfactory elemental analysis.

2.2 The Effect of Alkene and Epoxide Substituents on the Bromination Reaction.-

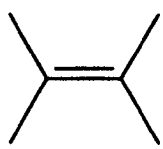
Having established reaction conditions which optimise production of dibromoether relative to the production of dibromide, it was decided to investigate the effect of substituent groups on both the alkene and epoxide components. The study was designed to define the scope and limitations of the reaction and to reveal its stereochemical consequences. The following commercially available alkenes were used in the study: *cis*-but-2-ene (VI), *trans*-but-2-ene (VII), 2-methylbut-2-ene (XLI), and 2,3-dimethylbut-2-ene (XXXIX).

(VI)

(VII)



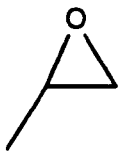
(XLI)



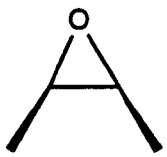
(XXXIX)

The study also utilized the following epoxides: ethylene oxide (XVIII), propylene oxide (XLII), *cis*-but-2-ene oxide (XX), *trans*-but-2-ene oxide (XXI), 2-methylbut-2-ene oxide (XLIII), and 2,3-dimethylbut-2-ene oxide (XLIV):

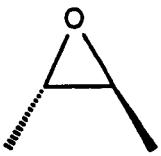
(XVIII)



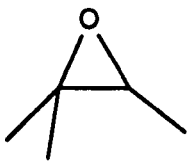
(XLII)



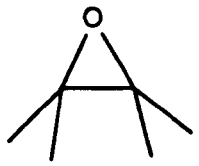
(XX)



(XXI)



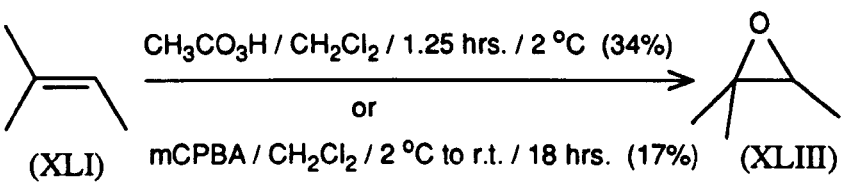
(XLIII)



(XLIV)

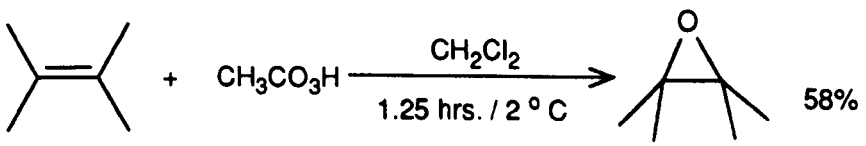
2.2.1 Preparation of epoxides.

Commercially available epoxides were used apart from 2-methylbut-2-ene oxide (XLIII) and 2,3-dimethylbut-2-ene oxide (XLIV). 2-Methylbut-2-ene oxide (XLIII) was prepared from 2-methylbut-2-ene (XLI) *via* oxidation with either peracetic acid or *meta*-chloroperbenzoic acid (*m*CPBA) (XLV) to leave the desired epoxide as a clear colourless liquid.



(XLI) (XLV) (XLIII)

2,3-Dimethylbut-2-ene oxide (XLIV) was prepared *via* the oxidation of 2,3-dimethylbut-2-ene (XXXIX) with peracetic acid in a similar manner.



(XXXIX) (XLIV)

2.2.2 The interaction of substituted alkenes with substituted epoxides.

The twenty-four reactions defined by the grid in Table 7 were carried out in order to define the scope of the reaction.

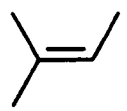
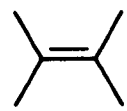
		EPOXIDE					
		 (XVIII)	 (XLII)	 (XX)	 (XXI)	 (XLIII)	 (XLIV)
ALKENE	 (VI)						
	 (VII)						
	 (XLI)						
	 (XXXIX)						

Table 7: Substituted alkenes and epoxides

All these reactions were carried out on the same scale and employed 2.5 mmol of alkene and 5 mmol of epoxide. Minor modifications were necessary depending on whether the reactants were:

a. both liquids,

b. both gases, or

c. one a liquid and the other a gas:

a. Epoxide and alkene both liquids at room temperature and pressure

The alkene was stirred with pentane in an acetone/carbon dioxide cooling bath. The epoxide was added. A solution of bromine in pentane was added to the reaction mixture portionwise over 1 hour. The resulting orange solution was allowed to warm to room temperature and washed, first with sodium thiosulphate solution and then with water. The organic phase was dried over magnesium sulphate, filtered and then concentrated *in vacuo* to leave the product mixture. The products were inspected by 220 MHz ^{1}H n.m.r. spectroscopy and the ratio of dibromoether to dibromide calculated by measuring the ratio of the integrals of the resonances due to the methyl protons of the two products.

b. Epoxide and alkene both gases at room temperature and pressure

A measured volume of gaseous alkene was condensed into a measuring cylinder sealed with a rubber septum and cooled to -78 °C. A known volume of pentane was added. An aliquot containing a known amount of alkene was then removed and stirred in pentane in an acetone/carbon dioxide cooling bath.

A measured volume of epoxide was then similarly condensed into a cooled, sealed measuring cylinder and diluted with pentane. An appropriate aliquot of this solution was added to the stirred reaction mixture. A solution of bromine in pentane was added to the reaction portionwise over 1 hour. The resulting orange solution was allowed to warm to room temperature and worked-up as before. The ratio of dibromoether to dibromide was calculated as above.

c. One reactant a liquid, and the other reactant a gas at room temperature and pressure

These reactions were carried out by the procedure used for the bromination of 2,3-dimethylbut-2-ene (XXXIX) [liquid] and ethylene oxide (XVIII) [gas] which was

described above.

The results from the reactions are given below in Table 8. The figures refer to the dibromoether component of the dibromoether(s)/dibromide ratio, i.e. for clarity a ratio of dibromoether:dibromide of 73:27 is represented as 73.

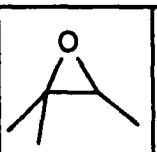
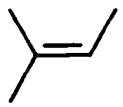
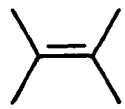
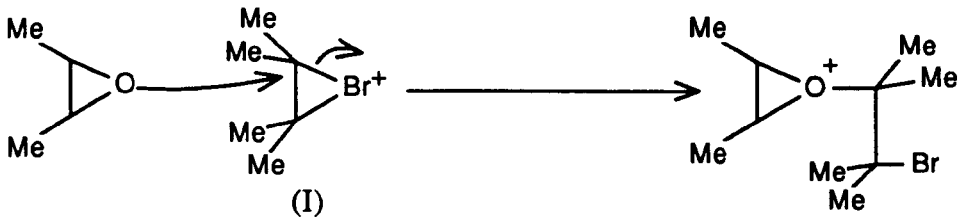
		EPOXIDE					
		 (XVIII)	 (XLII)	 (XX)	 (XXI)	 (XLIII)	 (XLIV)
ALKENE	 (VI)	73	85	59	55	38	5
	 (VII)	68	64	69	53	30	5
	 (XLI)	85	85	56	65	33	34
	 (XXXIX)	66	72	90	43	25	27

Table 8: Dibromoether component of dibromoether(s)/dibromide ratio obtained from alkene/epoxide brominations (measured by ^{1}H n.m.r. spectroscopy)

It can be seen from Table 8 that acceptable yields of dibromoethers are produced when epoxides (XVIII), (XLII), (XX), and (XXI) are used with alkenes (VI), (VII), (XLI), and (XXXIX). Although the sterically more hindered epoxides (XLIII) and (XLIV) gave some

dibromoether product, the reactions are of little synthetic value.

The results obtained on bromination of epoxide/2,3-dimethylbut-2-ene (XXXIX) mixtures (Table 8, row 4) are worthy of comment. As the level of epoxide substitution increases along the series (XVIII), (XLII) and (XX) so the proportion of dibromoether produced increases. This is attributed to the electron donating effect of the methyl substitutents which increase the nucleophilicity of the epoxide oxygen and thus encourage its attack on the bromonium ion (I).



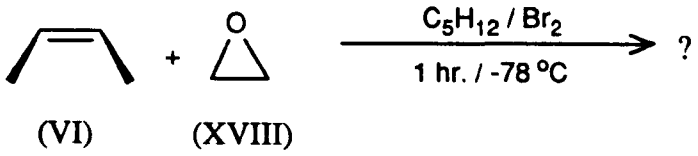
Scheme J

The resulting oxonium ion (Scheme J) is also stabilized by the electron donating substituents. For the remaining epoxides (XXI), (XLIII), and (XLIV) steric factors become important and start to hinder the approach of the epoxide to the bromonium ion thus favouring the formation of dibromide.

Having completed an initial survey of the bromination of alkene/epoxide mixtures, a detailed examination of eight of the reactions in Table 8 was carried out. The eight reactions were chosen to reveal the stereochemical consequences of bromination of alkene/epoxide mixtures.

2.2.2.1 The opening of the bromonium ion

The stereochemical consequences of the opening of the bromonium ion were studied by examination of the bromination of a mixture of *cis*-but-2-ene (VI)/ethylene oxide (XVIII) and a mixture of *trans*-but-2-ene (VII)/ethylene oxide (XVIII).

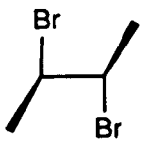


(VI) (XVIII)

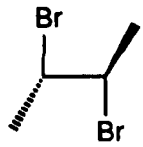
(VII) (XVIII)

A known volume of ethylene oxide (XVIII) was condensed into a cooled measuring cylinder sealed with a rubber septum and then diluted with a known volume of pentane. An aliquot containing 5 mmol of ethylene oxide (XVIII) was removed and stirred in pentane at -78 °C. A known volume of *cis*-but-2-ene (VI) was then condensed into a cooled, sealed measuring cylinder and diluted with pentane. An aliquot containing 2.5 mmol of butene (VI) was added to the reaction mixture. A solution of bromine in pentane was added to the stirred reaction mixture portionwise over 1 hour. The resulting orange solution was allowed to warm to room temperature and washed, first with sodium thiosulphate solution and then with water. Drying over magnesium sulphate, filtration, and concentration *in vacuo* furnished a clear, colourless liquid. Examination of the 400 MHz ^{1}H n.m.r. spectrum of this liquid revealed it to be a mixture of a dibromoether and dibromide (XLVI) in a ratio of 73:27.

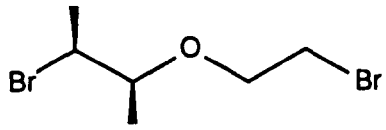
Repeating the experiment using *trans*-but-2-ene (VII) with ethylene oxide (XVIII) and work-up as before led to the isolation of a clear, colourless liquid. Examination of the 400 MHz ^{1}H n.m.r. spectrum revealed it to be a mixture of a dibromoether and dibromide (XLVII) in a ratio of 68:32.



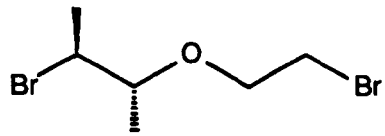
(XLVI)



(XLVII)



(XLVIII)



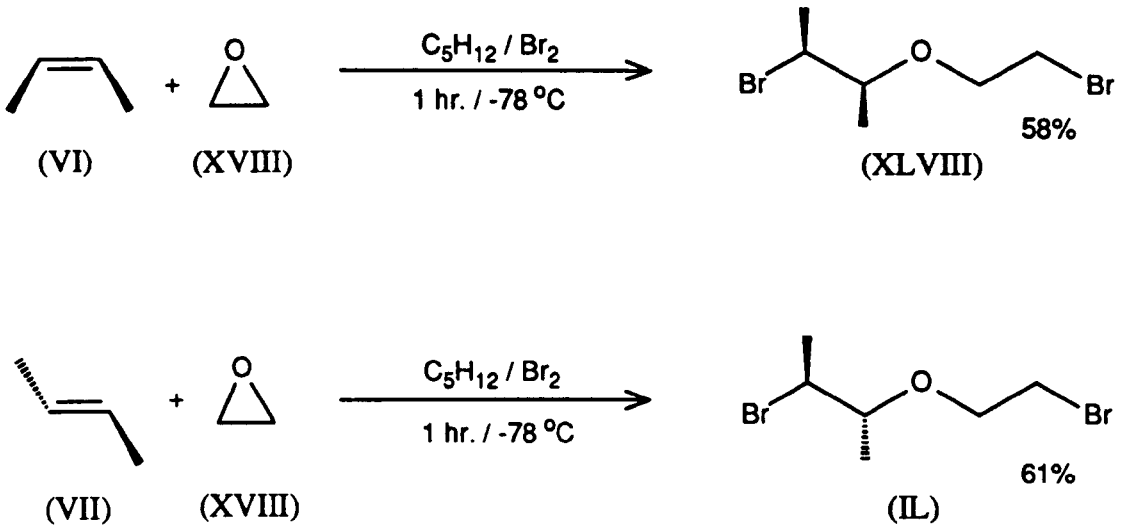
(IL)

In each of the reactions described above, the two diastereoisomeric dibromoethers (XLVIII) and (IL) are possible products. Inspection of the ^{13}C and ^{1}H n.m.r. spectra of the product mixture from the reaction of *cis*-but-2-ene (VI) with ethylene oxide (XVIII) revealed that two dibromoether products were present. The ratio of the dibromoethers, however, (based on resonances due to methyl protons [^{1}H] and methyl carbons [^{13}C]) was found to be >95:5. Similarly, the ^{13}C and ^{1}H n.m.r. spectra of the product mixture from the reaction of *trans*-but-2-ene (VII) with ethylene oxide (XVIII) revealed that two dibromoethers were present. In this case the ratio of dibromoethers was found to be reversed to <5:95. Each reaction, therefore, results in the formation of essentially one of the two possible diastereoisomeric dibromoethers.

Chromatography, and distillation *in vacuo* led to the isolation of the major dibromoether from each reaction as clear, colourless liquids (58%, b.p.$_{758.4}$ 220-223 °C [dec.], and 61%, b.p.$_{758.4}$ 236-239 °C [dec.], respectively).

Each reaction, above, results in the formation of essentially one product. The bromonium ions derived from *cis*- and *trans*-but-2-ene, (VI) and (VII), must, therefore, be opened by the oxygen atom of ethylene oxide (XVIII) under good stereochemical control. Assuming that the opening occurs with inversion of configuration (see introduction), then the product isolated from the *cis*-but-2-ene (VI)/ethylene oxide (XVIII) reaction is the novel β,

β′-dibromoether (XLVIII), and the product from *trans*-but-2-ene (VII)/ethylene oxide (XVIII) is its diastereoisomer (IL).



(VI) (XVIII) (XLVIII)

(VII) (XVIII) (IL)

n.b. in each case only one enantiomer is depicted for clarity.

The 400 MHz ^{1}H and 100.6 MHz ^{13}C n.m.r. spectral data for the isolated dibromoethers (XLVI) and (XLVII) is summarised in Table 9 overleaf.

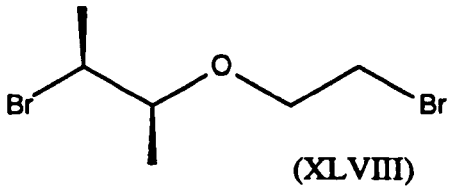
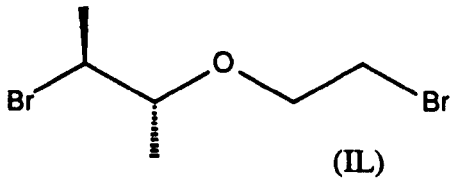
	 (XLVIII)	 (IL)
	^1H / δ	^1H / δ
-OCH(C<u>H</u>$_3$)-	1.22 (3H, d, *J* 6.3 Hz)	1.25 (3H, d, *J* 6.2 Hz)
BrCH(C<u>H</u>$_3$)-	1.62 (3H, d, *J* 6.8 Hz)	1.66 (3H, d, *J* 6.8 Hz)
BrC<u>H</u>$_2$-	3.41 (2H, t, *J* 6.2 Hz)	3.44 (2H, t, *J* 6.4 Hz)
-OC<u>H</u>(CH$_3$)-	3.56 (1H, dq, *J* 4.4 & 6.3 Hz)	3.49 (1H, dq, *J* 4.8 & 6.2 Hz)
-OC<u>H</u>$_2$-	3.73 (1H, dt, *J* 10.8 & 6.2 Hz)	3.80 (1H, dt, *J* 10.7 & 6.4 Hz)
	3.82 (1H, dt, *J* 10.8 & 6.2 Hz)	3.81 (1H, dt, *J* 10.7 & 6.4 Hz)
BrC<u>H</u>(CH$_3$)-	4.11 (1H, dq, *J* 4.4 & 6.8 Hz)	4.11 (1H, dq, *J* 4.8 & 6.8 Hz)
	^{13}C / δ	^{13}C / δ
-OCH(C<u>H</u>$_3$)-	15.8	17.1
BrCH(C<u>H</u>$_3$)-	20.3	21.4
BrC<u>H</u>$_2$-	30.4	30.4
BrC<u>H</u>(CH$_3$)-	51.4	52.8
-OC<u>H</u>$_2$-	69.4	69.5
-OC<u>H</u>(CH$_3$)-	79.1	79.7

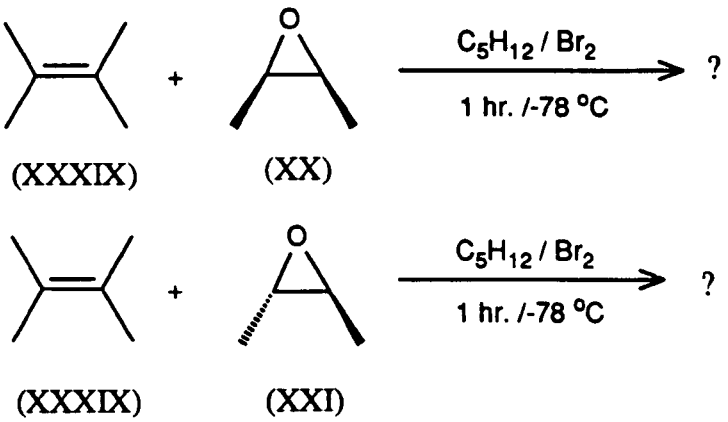
Table 9: 400 MHz ^1H n.m.r. and 100.6 MHz ^{13}C n.m.r. data for dibromoethers (XLVIII) and (IL)

The diastereoisomeric dibromoethers are readily distinguished by the resonances due to the methyl protons [doublets at δ 1.22 and δ 1.62 for (XLVIII) and at δ 1.25 and δ 1.66 for (IL)] in the ^1H n.m.r. spectra and by the resonances due to the methyl carbons [δ 15.8 and δ 20.3 for (XLVIII) and δ 17.1 and δ 21.4 for (IL)] in the ^{13}C n.m.r. spectra.

The mass spectrum and microanalytical data for each dibromoether were entirely consistent with the proposed structure of the products.

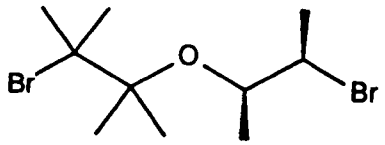
2.2.2.2 The opening of the epoxide

The stereochemical consequences of the opening of the epoxide were studied by examination of the bromination of a mixture of 2,3-dimethylbut-2-ene (XXXIX)/*cis*-but-2-ene oxide (XX) and a mixture of 2,3-dimethylbut-2-ene (XXXIX)/*trans*-but-2-ene oxide (XXI).

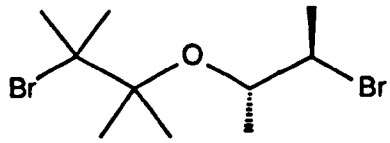


A solution of 2.5 mmol of 2,3-dimethyl-but-2-ene (XXXIX) in pentane was stirred at -78 °C in an acetone/carbon dioxide cooling bath. Two mole-equivalents of *cis*-but-2-ene oxide (XX) were added. A solution of bromine in pentane was added to the reaction mixture portionwise over 1 hour. The resulting orange solution was allowed to warm to room temperature and washed, first with sodium thiosulphate solution and then with water. Drying over magnesium sulphate, filtration and concentration *in vacuo* gave 'wet' white crystals. The 400 MHz ^{1}H n.m.r. spectrum of these crystals revealed that the ratio of dibromoether produced to dibromide (V) was 90:10.

Repeating the experiment with *trans*-but-2-ene oxide (XXI) and 2,3-dimethylbut-2-ene (XXXIX) and work-up as before again led to the isolation of 'wet' white crystals. Examination of the 400 MHz ^{1}H n.m.r. spectrum revealed that the ratio of dibromoether to dibromide (V) was 43:57.



(L)

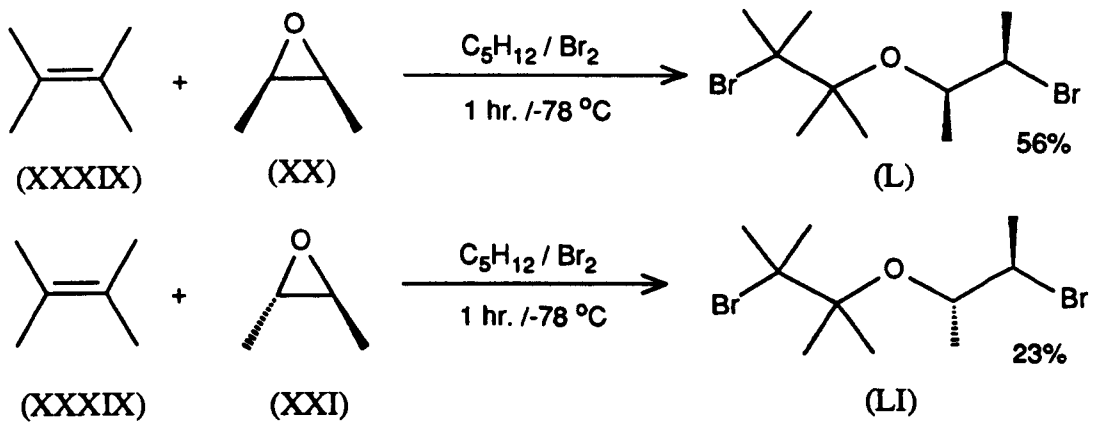


(LI)

The two reactions described above could both give two diastereoisomeric dibromoethers (L) and (LI) as products. Examination of the ^{13}C and ^{1}H n.m.r. spectra of the product mixture obtained from the reaction of the alkene (XXXIX) with the *cis*-epoxide (XX) revealed that two dibromoether products were present but in a ratio of >95:5. The spectra from the reaction of the alkene (XXXIX) with the *trans*-epoxide (XXI) indicated that both dibromoethers were again present but this time the ratio was reversed to <95:5. Each reaction results therefore in the formation of essentially one different dibromoether product with a selectivity of >95:5 in each case.

Chromatography, and distillation *in vacuo* allowed the separation of the major dibromethers from each reaction as clear, colourless liquids (56%, b.p.$_{744.6}$ 152-154 °C [dec.], and 23%, b.p.$_{770.8}$ 168-170 °C [dec.] respectively).

The reactions described above both result in the formation of essentially one dibromoether and thus, the opening of the epoxide occurs under good stereochemical control. Assuming that the control over the opening of the epoxides is achieved by an S_N2-type process (see introduction) then the β,β′-dibromoether isolated from the 2,3-dimethylbut-2-ene (XXXIX)/*cis*-but-2-ene oxide (XX) reaction is the novel β,β′-dibromoether (L) and that from 2,3-dimethylbut-2-ene (XXXIX)/*trans*-but-2-ene oxide (XXI) is its diastereoisomer (LI):



n.b. in each case only one enantiomer is depicted for clarity

The 400 MHz ^1H n.m.r. and 100.6 MHz ^{13}C n.m.r. spectra data for the isolated dibromoethers (L) and (LI) is summarised in Table 10 overleaf.

The two diastereoisomeric dibromoethers (L) and (LI) are readily distinguished in the ^1H n.m.r spectra by the $-OC(C\underline{H}_3)_2-$ and $BrC(C\underline{H}_3)_2-$ signals [singlets at δ 1.33, 1.35, 1.77 and 1.78 for (L), and δ 1.36, 1.37, 1.80 and 1.81 for (LI)].

The mass spectrum and microanalytical data for each β,β′-dibromoether were entirely consistent with their proposed structure.

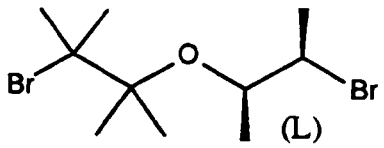
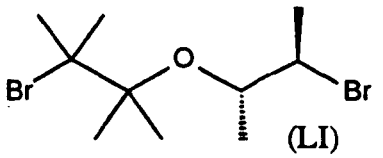
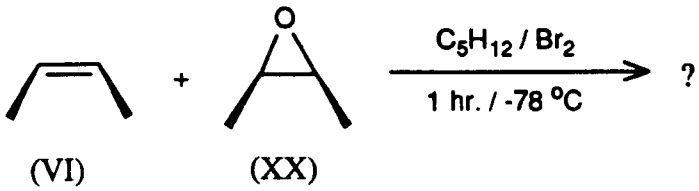
	 (L)	 (LI)
	^1H / δ	^1H / δ
-OCH(C<u>H</u>$_3$)-	1.22 (3H, d, *J* 6.2 Hz)	1.21 (3H, d, *J* 6.1 Hz)
-OC(C<u>H</u>$_3$)$_2$-	1.33 (3H, s)	1.36 (3H, s)
	1.35 (3H, s)	1.37 (3H, s)
BrCH(C<u>H</u>$_3$)-	1.62 (3H, d, *J* 6.8 Hz)	1.63 (3H, d, *J* 6.9 Hz)
BrC(C<u>H</u>$_3$)$_2$-	1.77 (3H, s)	1.80 (3H, s)
	1.78 (3H, s)	1.81 (3H, s)
-0C<u>H</u>(CH$_3$)-	3.90 (1H, dq, *J* 3.7 & 6.2 Hz)	3.68 (1H, dq, *J* 4.4 & 6.1 Hz)
BrC<u>H</u>(CH$_3$)-	4.07 (1H, dq, *J* 3.7 & 6.8 Hz)	4.06 (1H, dq, *J* 4.4 & 6.9 Hz)
	^{13}C / δ	^{13}C / δ
-OCH(C<u>H</u>$_3$)-	16.3	19.7
BrCH(C<u>H</u>$_3$)-	18.9	21.8
-OC(C<u>H</u>$_3$)$_2$-	21.7	21.8
	22.0	22.6
BrC(C<u>H</u>$_3$)$_2$-	29.6	29.7
	29.7	29.8
Br<u>C</u>H(CH$_3$)-	52.1	55.8
-O<u>C</u>H(CH$_3$)-	70.1	71.7
Br<u>C</u>H(CH$_3$)$_2$-	73.9	74.4
-O<u>C</u>H(CH$_3$)$_2$-	80.2	80.2

Table 10: 400 MHz ^1H n.m.r. and 100.6 MHz ^{13}C n.m.r. data for dibromoethers (L) and (LI)

2.2.2.3 The approach of the epoxide and the bromonium ion

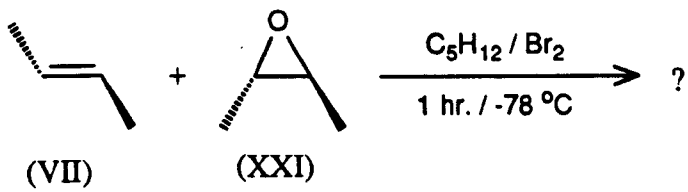
Experiments were carried out to determine the relative stereochemistry of products containing chiral centres at the α-, α′-, β- and β′-carbon atoms. A bromine solution was added to each of the four mixtures (a)-(d):

a. *cis*-but-2-ene (VI) / *cis*-but-2-ene oxide (XX)



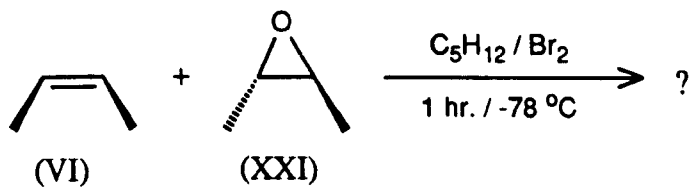
(VI) (XX)

b. *trans*-but-2-ene (VII) / *trans*-but-2-ene oxide (XXI)



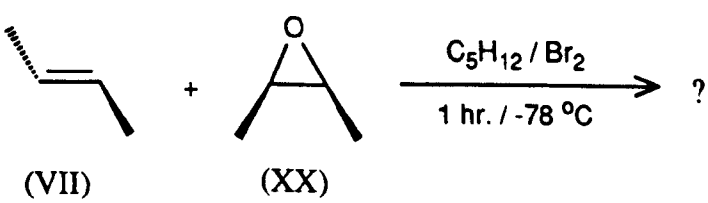
(VII) (XXI)

c. *cis*-but-2-ene (VI) / *trans*-but-2-ene oxide (XXI)



(VI) (XXI)

d. *trans*-but-2-ene (VII) / *cis*-but-2-ene oxide (XX)



(VII) (XX)

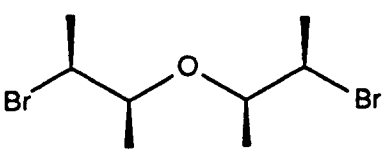
cis-But-2-ene oxide (XX) was stirred in pentane in an acetone/carbon dioxide cooling bath. A known volume of *cis*-but-2-ene (VI) was condensed into a cooled, sealed measuring cylinder, and then diluted with pentane. An aliquot containing 0.5 mole-equivalents of *cis*-but-2-ene (VI) was added to the reaction mixutre. A solution of bromine in pentane was added to the reaction portionwise over 1 hour. The resulting orange solution was allowed to warm to room temperature and then washed, first with sodium thiosulphate solution and then with water. Drying over magnesium sulphate, filtration and concentration *in vacuo* gave a clear, colourless liquid. The 400 MHz ^{1}H n.m.r. spectrum of this liquid revealed that it was a 59:41 mixture of two dibromoethers and the dibromide (XLVI). The ratio of the two dibromoethers was 1:1, and the ratio of these two major diastereoisomers to other diastereoisomers was >95:5.

The same procedure was followed with the other reagent pairs [(b)-(d)] to give the results summarised in Table 11.

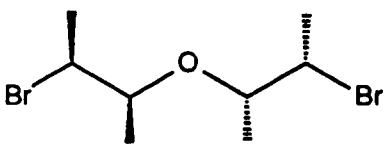
Reagent Pair	Ratio of Dibromoethers : Dibromide	Ratio of two Major Diastereoisomers	Ratio of Major : Minor Diastereoisomers
(a)	59:41	1:1	> 95:5
(b)	53:47	1:1	> 95:5
(c)	55:45	2:1	> 95:5
(d)	69:31	1:3	> 95:5

Table 11: Results of brominations of reagent pairs (a) - (d)

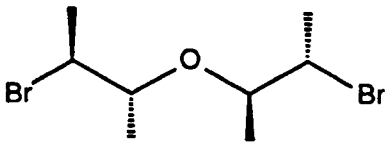
If no stereochemical control was exercised over the brominations of reactant pairs (a) - (d), each reaction would produce a mixture of all six possible dibromoethers (LII) to (LVII):



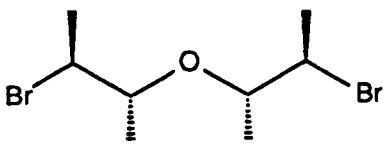
(LII)



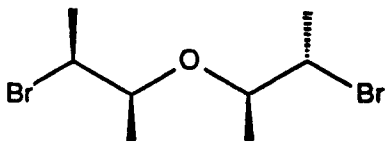
(LIII)



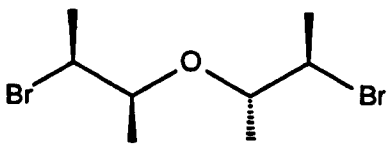
(LIV)



(LV)



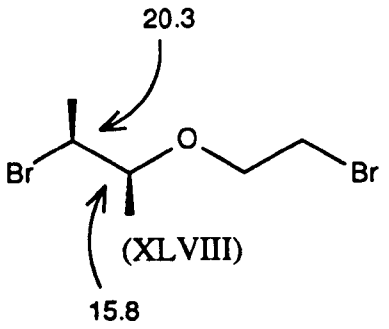
(LVI)

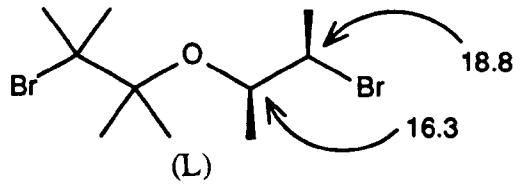


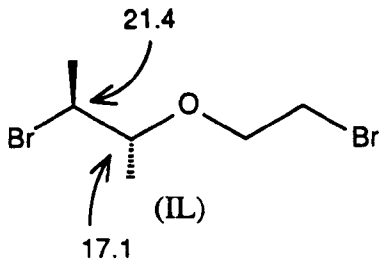
(LVII)

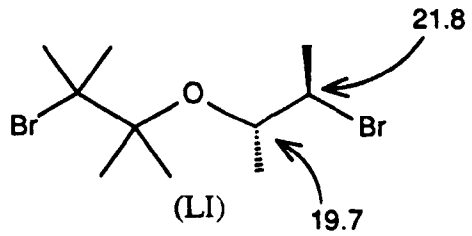
n.b. one enantiomer of each structure is depicted for clarity.

In fact, in each case only two diastereoisomeric dibromoethers were obtained. The crude products from the above reactions were purified by chromatography and distillation *in vacuo* to isolate the two major diastereoisomers from each reaction. For example, purification of the crude product from reaction (a) [*cis*-but-2-ene (VI)/*cis*-but-2-ene oxide (XX)] produced a mixture of two dibromoethers in 61% yield as clear, colourless liquids. The structures of these dibromoethers were assigned by assuming good stereochemical control over the opening of the bromonium ion and epoxide (see Sections 2.2.2.1 and 2.2.2.2) and poor control over the approach of the epoxide and the bromonium ion. The ^{1}H n.m.r. and ^{13}C n.m.r. spectra of the dibromoether mixture were consistent with these assumptions. Examination of the ^{13}C n.m.r. spectra of dibromoethers (XLVIII) and (L) which both have methyl substituents in a *cis*-arrangement suggests that $BrCH(\underline{C}H_3)$-carbon atoms produce a resonance at about δ 19.5 and $-OCH(\underline{C}H_3)$- carbon atoms produce a resonance at about δ 16 when these groups are *cis*- to one another.

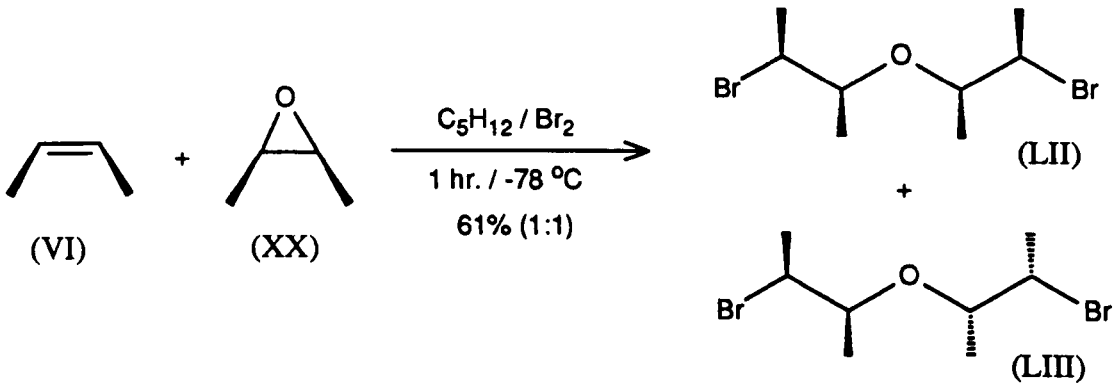




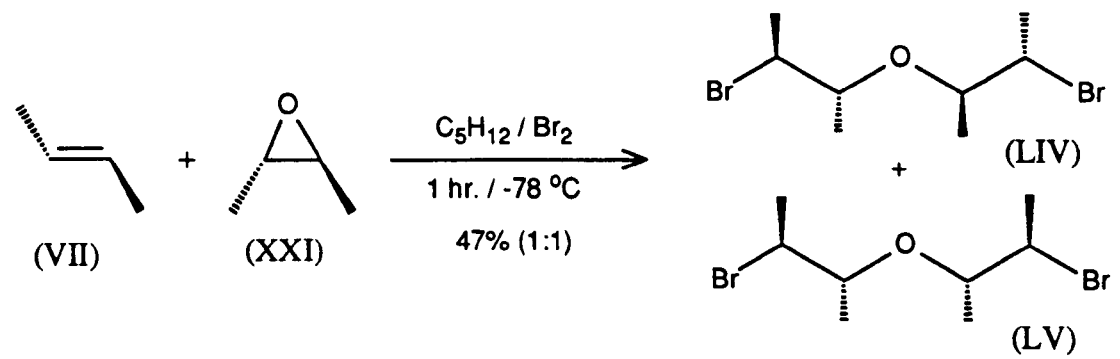




Examination of the ^{13}C n.m.r. spectra of dibromoethers (IL) and (LI) which have methyl substituents in a *trans*-arrangement, however, suggests that $BrCH(\underline{C}H_3)$- carbon atoms produce a resonance at about δ 21.6 and $-OCH(\underline{C}H_3)$- carbon atoms produce a resonance at about δ 18.5 when the methyls are *trans*- to one another. In the case of reaction (a) [*cis*-but-2-ene (VI)/*cis*-but-2-ene oxide (XX)], opening of the bromonium ion formed from bromination of (VI) would be expected to give a *cis*-arrangement of methyl groups in the product (see section 2.2.2.1). Opening of epoxide (XX) by bromide ion would again be expected to give a *cis*-arrangement of methyl groups in the product (see section 2.2.2.2). The ^{13}C n.m.r. spectrum gave shifts due to methyl carbon resonances at δ 20.2, 20.0, 16.2 and 15.9 in better agreement with the shifts predicted from '*cis*-dibromoethers' (XLVIII) and (L) [δ 19.5 and δ 16] than from '*trans*-dibromoethers' (IL) and (LI) [δ 21.6 and 18.5]. Predictions from earlier reactions, and ^{13}C n.m.r. spectral data, therefore, are entirely consistent with the two major β,β′-dibromoethers produced from reaction (a) being '*cis-cis*'-compounds (LII) and (LIII).

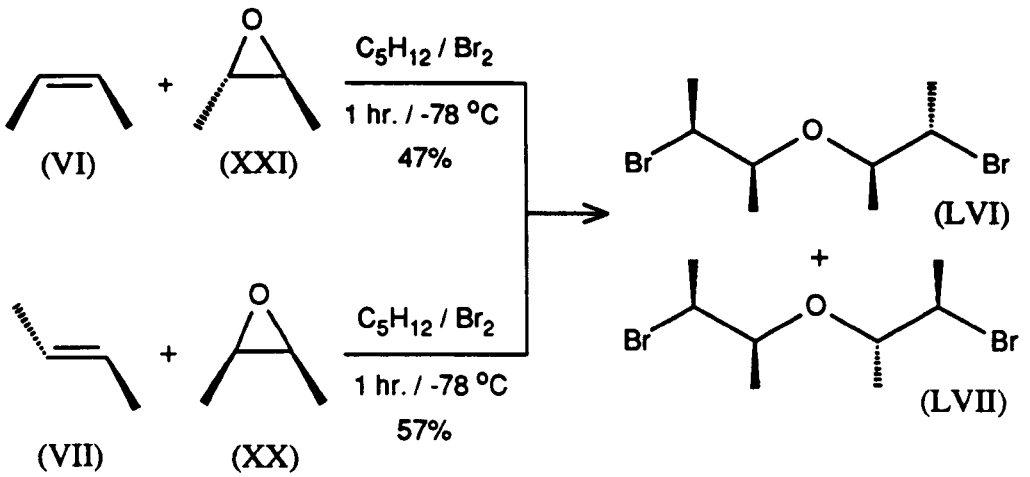


Predictions of the stereochemistry of the β,β′-dibromoethers produced from reaction (b) [*trans*-but-2-ene (VII)/*trans*-but-2-ene oxide (XXI)] suggest a *trans-trans*-arrangement of methyl groups in the product. The ^{13}C n.m.r. sprectrum of the purified dibromoethers obtained from this reaction show shifts due to methyl carbons at δ 21.8, 21.3, 18.1 and 17.5 which are in better agreement with the shifts obtained from '*trans*-dibromoethers' (IL) and (LI) [δ 21.6 and 18.5] than those from '*cis*-dibromoethers' (XLVIII) and (L) [δ 19.5 and 16]. The results, therefore, are consistent with the two major β,β′-dibromoethers from reaction (b) being '*trans-trans*'-compounds (LIV) and (LV)



Similarly, data on the β,β′-dibromoethers isolated from reactions (c) [*cis*-but-2-ene (VI)/*trans*-but-2-ene oxide (XXI)] and (d) [*trans*-but-2-ene (VII)/*cis*-but-2-ene oxide (XX)] were consistent with the dibromoethers obtained being '*cis-trans*'-compounds (LVI) and (LVII). Chromatography and distillation *in vacuo* allowed the isolation of β,β′-dibromoethers (LVI) and (LVII) as clear, colourless liquids from reaction (c) in 47%

yield, and from reaction (d) in 57% yield. The ratio of the two dibromoethers from reaction (c) was 2:1 while the ratio of the same dibromoethers from reaction (d) was reversed to 1:3.



The full 400 MHz ^1H n.m.r. and 100.6 MHz ^{13}C n.m.r. spectral data for β,β′-dibromoethers (LII) - (LVII) is summarised in Table 12 overleaf.

The mass spectra of the β,β′-dibromoethers were entirely consistent with the proposed structures.

The results described above reveal that the approach of the epoxide and the bromonium ion is weakly controlled in cases (c) and (d), and not controlled at all in cases (a) and (b).

2.2.3 The attack of the epoxide on the bromonium ion.

The formation of β,β′-dibromoethers from the bromination of alkene/epoxide mixtures may be accounted for by Scheme I, a variation on the intramolecular bromination of cyclic epoxyalkenes (see Scheme H).

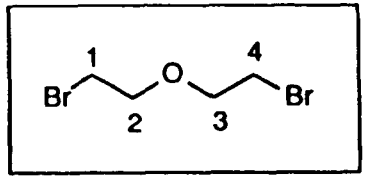
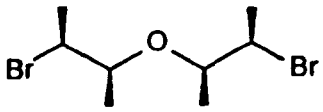
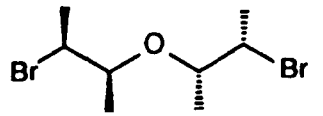
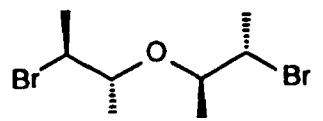
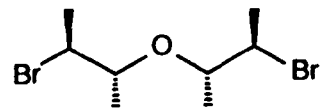
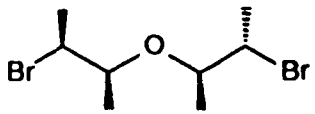
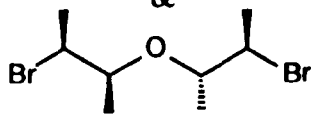


Table 12a: 400 MHz ^{1}H n.m.r. data for β,β'-dibromoethers (LII) to (LVII).

	PROTON /δ [*J* value /Hz]							
	$C_1\underline{H}$	$C_2\underline{H}$	$C_3\underline{H}$	$C_4\underline{H}$	$C_1C\underline{H}_3$	$C_2C\underline{H}_3$	$C_3C\underline{H}_3$	$C_4C\underline{H}_3$
 (LII) &  (LIII)	4.08 (dq) [4.3, 6.8] 4.10 (dq) [4.7, 6.8]	3.65 (dq) [4.3, 6.3] 3.67 (dq) [4.7, 6.8]	As $C_1\underline{H}$	As $C_2\underline{H}$	1.61 (d) [6.8] 1.63 (d) [6.8]	1.21 (d) [6.3] 1.22 (d) [6.3]	As $C_2C\underline{H}_3$	As $C_1C\underline{H}_3$
 (LIV) &  (LV)	4.11 (dq) [4.7, 6.9] 4.06 (dq) [4.7, 6.8]	3.57 (dq) [4.7, 6.2] 3.59 (dq) [4.7, 6.2]	As $C_1\underline{H}$	As $C_2\underline{H}$	1.67 (d) [6.9] 1.64 (d) [6.8]	1.22 (d) [6.2] 1.25 (d) [6.2]	As $C_2C\underline{H}_3$	As $C_1C\underline{H}_3$

 (LVI) &  (LVII)	4.08 or 3.60 (dq) (dq) [4.9, [4.9, 6.8] 6.2] or or 4.11 or 3.71 (dq) (dq) [4.4, [4.4, 6.8] 6.3]	3.60 or 4.08 (dq) (dq) [4.9, [4.9, 6.2] 6.8] or or 3.71 or 4.11 (dq) (dq) [4.4, [4.4, 6.3] 6.8]	1.65 (d) [6.6] or 1.67 (d) [6.6]	1.26 (d) [6.4] or 1.28 (d) [6.6]		
n.b. first data is for the major diastereoisomer in reaction (c)	4.06 or 3.58 (dq) (dq) [4.3, [4.3, 6.8] 6.2] or or 4.17or 3.69 (dq) (dq) [4.1, [4.1, 6.8] 6.3]	3.58 or 4.06 (dq) (dq) [4.3, [4.3, 6.2] 6.8] or or 3.69 or 4.17 (dq) (dq) [4.1, [4.1, 6.3] 6.8]	1.66 (d) [6.8] or 1.68 (d) [6.8]	1.24 (d) [6.2] or 1.25 (d) [6.3]	As $C_2\underline{C}H_3$	As $C_1\underline{C}H_3$

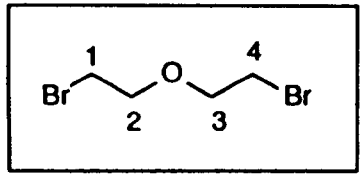
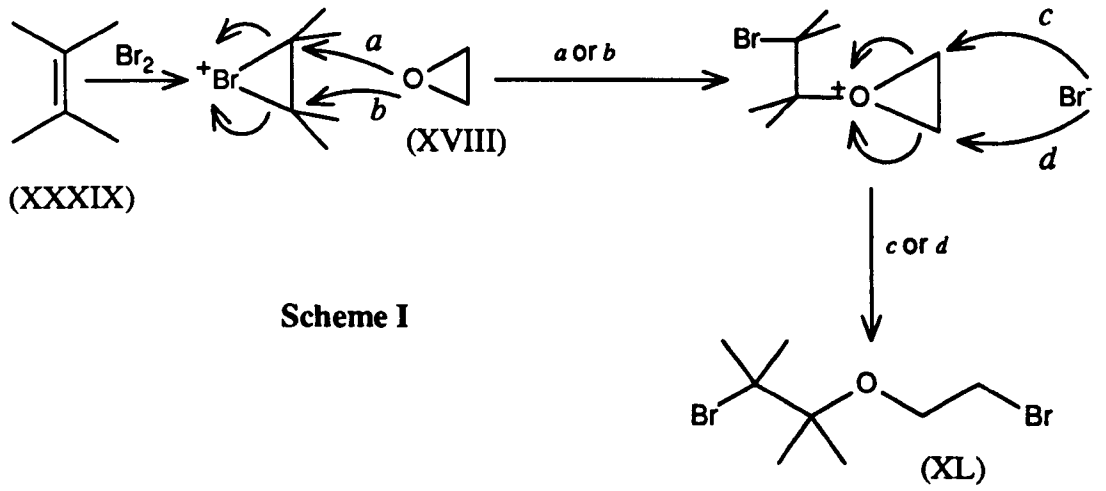


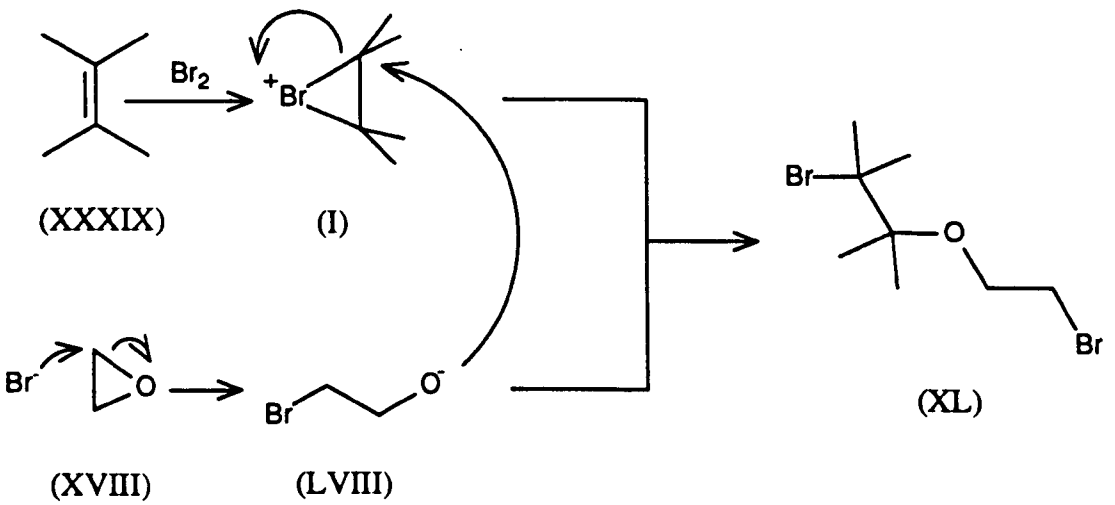
Table 12b: 100.6 MHz ^{13}C n.m.r. data for β,β'-dibromoethers (LII) to (LVII)

	CARBON /δ							
	$\underline{C}_1$	$\underline{C}_2$	$\underline{C}_3$	$\underline{C}_4$	$C_1\underline{C}H_3$	$C_2\underline{C}H_3$	$C_3\underline{C}H_3$	$C_4\underline{C}H_3$
(LII) & (LIII)	51.7 51.4	77.3 77.2	77.3 77.2	51.7 51.4	20.2 20.0	15.9 16.2	15.9 16.2	20.2 20.0
(LIV) & (LV)	53.6 53.5	78.1 77.5	78.1 77.5	53.6 53.5	21.8 21.3	18.1 17.5	18.1 17.5	21.8 21.3
(LVI) & (LVII)	51.1 51.1	77.2 77.3	77.6 78.0	51.8 53.3	20.1 19.8	15.7 16.0	17.7 18.0	21.4 21.1



Scheme I

The following mechanism may also be invoked to account for product formation (Scheme K):

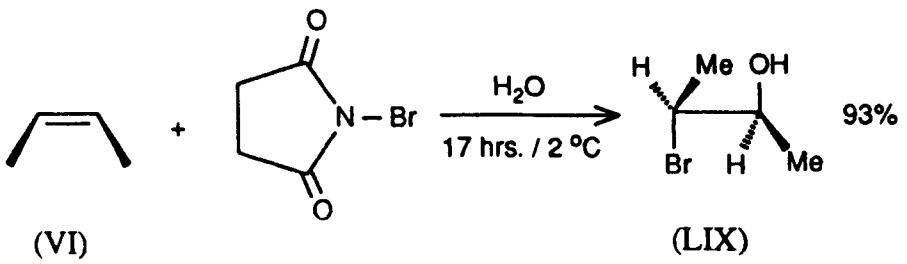


Scheme K

Nucleophilic attack on the epoxide by bromide ion forms the nucleophilic oxygen anion (LVIII). The anion (LVIII) then opens bromonium ion (I), to give the product (XL). Bromohydrin (LIX) was prepared in order to determine whether bromohydrins may be used in place of epoxides for the formation of dibromoethers.

2.2.3.1 Preparation of bromohydrin (LIX)[26]

N-Bromosuccinimide was cooled in an ice-water cooling bath and a large excess of ice added to it. *cis*-Butene (VI) was condensed into a cooled, sealed measuring cylinder and added to the reaction. The reaction mixture was stirred for 17 hours and then extracted with diethyl ether. Drying over magnesium sulphate, filtration and concentration *in vacuo* left bromohydrin (LIX) as a clear, colourless liquid, $b.p._{758.6}$ 153-154 °C, in 93% yield. The i.r. spectrum of the product contained an O-H stretch at 3 446 cm^{-1}, a C-H stretch at 2 979 cm^{-1}, and a CH_3-C stretch at 1 380 cm^{-1}. The 400 MHz ^1H n.m.r. spectrum contained two three-proton doublets at δ 1.16 [*J* 6.3 Hz, -CH(OH)CH_3-] and 1.61 [*J* 6.8 Hz, CHBr(CH_3)-], a one-proton singlet at δ 2.77 which was removable by shaking with D_2O (COH), and two one-proton doublets of quartets at δ 3.62 [*J* 6.3 and 3.8 Hz, CH(OH)-] and at δ 3.99 (*J* 6.8 and 3.9 Hz, Br CH-).



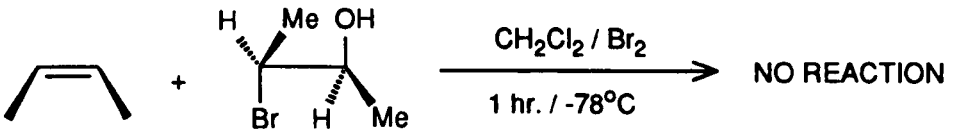
(VI) (LIX)

2.2.3.2 Bromination of alkene/bromohydrin mixtures

The bromohydrin (LIX) was then used instead of an epoxide in the bromination of *cis*-but-2-ene (VI) and of *trans*-but-2-ene (VII).

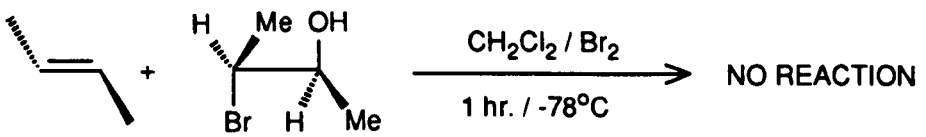
A known volume of *cis*-but-2-ene (VI) was condensed into a cooled, sealed measuring cylinder and diluted with a known volume of dichloromethane. [Bromohydrin (LIX) was insoluble in pentane and so reactions had to be carried out in dichloromethane, in order to solubilize (LIX)]. An aliquot containing 2.5 mmol was removed, diluted with dichloromethane and stirred in an acetone/carbon dioxide cooling bath. Following the addition of 2 mole-equivalents of bromohydrin (LIX), a solution of bromine in dichloromethane was added to the reaction mixture portionwise over 1 hour. The resulting

red liquid was allowed to warm to room temperature and washed, first with sodium thiosulphate solution and then with water. Drying over magnesium sulphate, filtration, and concentration *in vacuo* left a pale yellow liquid. The 400 MHz ^{1}H n.m.r. spectrum of this liquid revealed that the product was a mixture of unreacted bromohydrin (LIX) and dibromide (XLVI) in a ratio of 64:36. Distillation *in vacuo* furnished recovered bromohydrin (LIX) in 86% yield as a clear, colourless liquid. The b.p. and the ^{1}H n.m.r. and i.r. spectra were in good agreement with those obtained from the starting material.



(VI) (LIX)

Repeating the above reaction with *trans*-but-2-ene (VII) again produced a pale yellow liquid which was identified by 400 MHz ^{1}H n.m.r. spectroscopy a mixture of unreacted bromohydrin (LIX) and dibromide (XLVII) in a ratio of 45:55. Distillation *in vacuo* led to the recovery of bromohydrin (LIX) as a clear, colourless liquid (78%). The b.p. and ^{1}H n.m.r. and i.r. spectra were again in good agreement with the starting material.

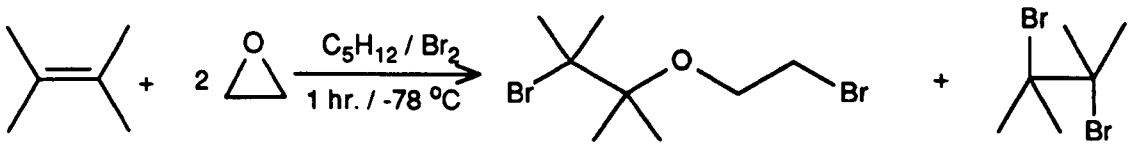


(VII) (LIX)

Thus, there was no reaction between bromohydrin (LIX) and the bromonium ion formed on the bromination of either *cis*- or *trans*-but-2-ene [(VI) and (VII)] under the conditions of the reaction.

2.3 Conclusions.-

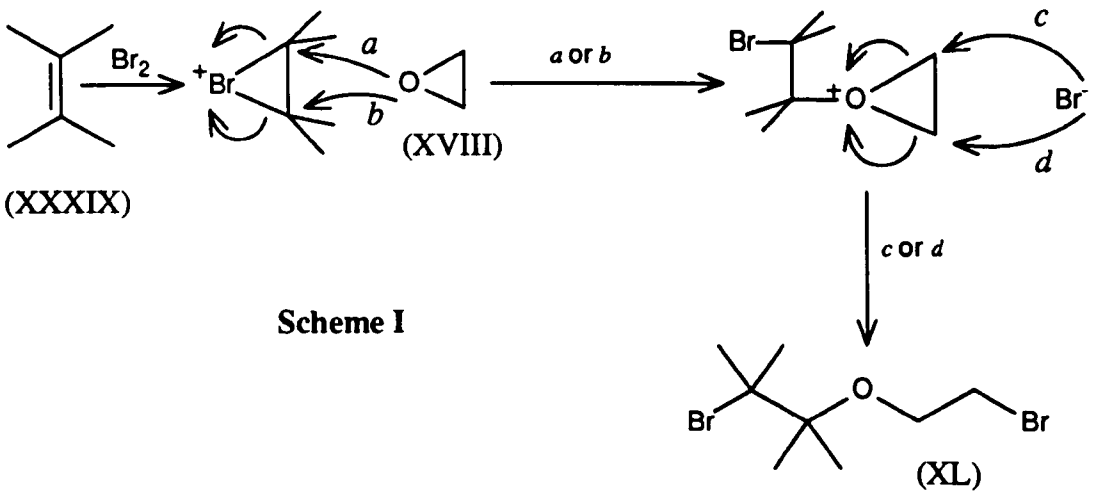
The bromination of alkene/epoxide mixtures leads to the formation of β,β′-dibromoethers and dibromoalkanes. The amount of β,β′-dibromoether formed was optimised relative to the amount of dibromoalkane formed by carrying out the reaction in pentane at -78 °C.



(XXXIX) (XVIII) (XL) (IV)

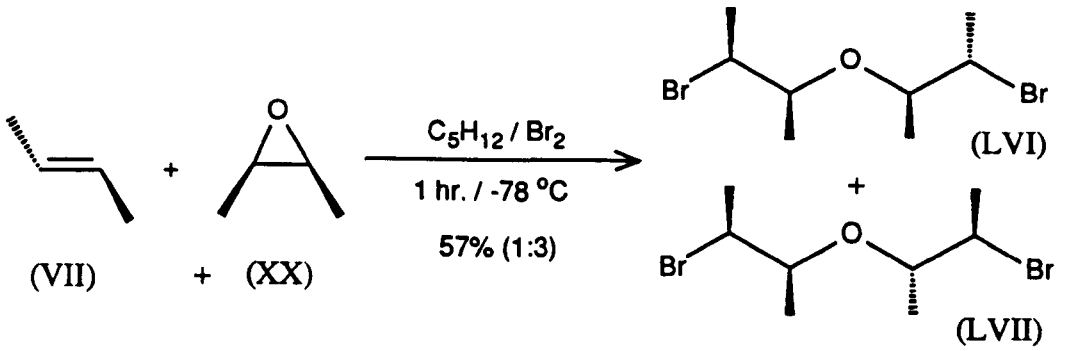
(67:33)

The reaction is believed to proceed *via* the mechanism shown below in Scheme I:



Scheme I

The opening of the bromonium ion (Step 2) and the opening of the epoxide (Step 3) have been shown to occur stereospecifically. Little control has been exerted, however, over the approach of the epoxide to the bromonium ion. Nevertheless, the bromination of but-2-ene/but-2-ene oxide mixtures leads to the formation of only two of six possible diastereoisomeric dibromoethers as exemplified by the reaction between alkene (VIII) and epoxide (XX) depicted overleaf.



(VII) + (XX)

EXPERIMENTAL

General Experimental.

Column chromatography was performed using Merck Kieselgel 60 (230-400 mesh) silica.

Petroleum ether (40-60) was distilled and refers to the fraction boiling between 40 and 60°C.

N.m.r. spectra were recorded on a Perkin Elmer R34 (220 MHz, ^{1}H) or Bruker WH400 (400 MHz, ^{1}H; 100.6 MHz, ^{13}C) instrument using tetramethylsilane as internal standard. *Mass spectra* were recorded on a Kratos MS 80 instrument at 70 eV, using chemical ionisation (C.I.) (NH_3), and electron ionisation (E.I.) techniques.

Elemental analyses were performed by MEDAC Ltd, Brunel University Chemistry Department.

2-Methylbut-2-ene Oxide (XLIII).-

a. <u>using peracetic acid</u>

Peracetic acid solution (40% in acetic acid, 16.83 ml, 100 mmol) was saturated with hydrated sodium acetate. 2-Methylbut-2-ene (XLI) (7.01 g, 100 mmol) was diluted with a solution of sodium carbonate (anhydrous, 10.59 g, 100 mmol) in dichloromethane (15 ml) and stirred in an ice-water cooling bath. The peracetic acid solution was added dropwise over 0.5 hours. The reaction mixture was stirred for 0.75 hours and then diluted with water (25 ml). Extraction with dichloromethane (3 x 20 ml) followed by drying over magnesium sulphate and filtration left a colourless

liquid, which was distilled *in vacuo* to remove the solvent and then isolate the title compound (XLIII) as a clear, colourless liquid (2.93 g, 34 %), b.p. 71-73 °C at 743.8 mm Hg^{-1} [lit.[27] 72-75 °C] $\upsilon_{max.}$ (neat) 3 000 - 2 900 (CH), and 1 080 cm^{-1} (C-O-C); δ_H (220 MHz; $CDCl_3$) 1.20 (3H, d, *J* 6 Hz, $CH(C\underline{H}_3)$), 1.25 (6H, s, 2 x $-C\underline{H}_3$), and 2.71 (1H, q, *J* 6 Hz, $C\underline{H}(CH_3)$) [lit.[27] (100 MHz; $CDCl_3$) 1.23 (3H, d), 1.27 (6H, s) and 2.80 (1H, q)].

b. using *meta*-chloroperbenzoic acid (XLV)

meta-Chloroperbenzoic acid (50%, 3.65 g, 10.6 mmol) was suspended in dichloromethane (25 ml) and stirred in an ice-water cooling bath. 2-Methylbut-2-ene (XLI) (0.72 g, 10.3 mmol) was added in one portion, the reaction allowed to warm up to room tempterature and then stirred for 18 hours. The resulting white suspension was diluted with dichloromethane (20 ml) and washed with sodium hydroxide solution (10%, 10 ml). The organic layer was washed with water (distilled) until the washings were neutral to Universal Indicator paper (4 x 50 ml), dried over magnesium sulphate, and then filtered. Distillation *in vacuo* allowed the removal of solvent and then the isolation of the title compound (XLIII) as a colourless liquid (0.15 g, 17%) b.p. 72-74 °C at 743.8 mm Hg [lit.[27] 72-75 °C], $\upsilon_{max.}$ (neat) 3 010 - 2 900 (CH) and 1 082 cm^{-1} (C-O-C); δ_H (220 MHz; $CDCl_3$) 1.21 (3H, d, *J* 6 Hz, $CH(C\underline{H}_3)$), 1.25 (6H, s, 2 x $-C\underline{H}_3$), and 2.69 (1H, q, *J* 6 Hz, $C\underline{H}(CH_3)$) [lit.[27] (100 MHz; $CDCl_3$) 1.23 (3H, d), 1.27 (6H, s) and 2.80 (1H, q)].

2,3-Dimethylbut-2-ene Oxide (XLIV).-

2,3-Dimethylbut-2-ene (XXXIX) (3.25 ml, 2.70 g, 33.0 mmol) was diluted with a solution of sodium carbonate (3.50 g, 33.0 mmol) in dichloromethane (15 ml) and stirred in an ice-water cooling bath. Peracetic acid solution (40% in acetic acid, 5.55 ml, 33 mmol) was saturated with hydrated sodium acetate and then added to the alkene solution

dropwise over 0.5 hours. The reaction mixture was allowed to warm to room temperature and stirred for a total of 19 hours before being diluted with water (distilled, 50 ml). The organic layer was washed with sodium carbonate solution (2%, 3 x 50 ml) and brine (2%, 3 x 50 ml). The aqueous layers were backwashed with dichloromethane (10 ml) and then the combined organic phases dried over magnesium sulphate and filtered. The resulting liquid was distilled *in vacuo* to remove the solvent and then isolate the title compound (XLIV) as a colourless liquid (1.86 g, 58%), b.p. 90-91 °C at 752.6 mm Hg [lit.[27] 90-93 °C]; $\upsilon_{max.}$ (neat) 2 980 - 2 950 (CH), and 1 140 cm^{-1} (C-O-C); δ_H (220 MHz; $CDCl_3$) 1.33 (12H, s, 4 x -$C\underline{H}_3$) [lit.[27] (100 MHz; $CDCl_3$) 1.32 (12H, s)].

BROMINATION OF ALKENE/EPOXIDE MIXTURES.-

These reactions were carried out by one of three methods.

Method A

This method was used when both the alkene and the epoxide were liquids at room temperature and pressure.

Alkene (2.5 mmol) was stirred with pentane (5 ml) in an acetone/carbon dioxide cooling bath. Epoxide (5.0 mmol) was added in one portion. A solution of bromine (3.1 mmol) in pentane (2.5 ml) was placed in a dropping funnel and added to the stirred reaction mixture portionwise over 1 hour. The resulting orange solution was allowed to warm to room temperature and then washed, first with sodium thiosulphate solution (2%, 25 ml) and then with water (distilled, 3 x 50 ml). The aqueous phases were backwashed with pentane (10 ml). The combined organic phases were dried over magnesium sulphate, filtered, and then concentrated *in vacuo* to leave the crude products, a mixture of β,β'-dibromoether(s) and dibromide which was analysed by ^1H n.m.r. spectroscopy. Chromatography on silica using 40-60 petroleum ether:dichloromethane (3:1) as eluent and distillation *in vacuo*

furnished β,β'-dibromoether(s) as a clear, colourless liquid.

Method B

This method was used when both alkene and the epoxide were gases at room temperature and pressure.

A 10 ml measuring cylinder with a ground-glass stopper was sealed with a rubber septum and cooled in an acetone/carbon dioxide cooling bath. A measured volume of alkene was then condensed into the measuring cylinder. Pentane was added to the condensed alkene using a syringe. An aliquot containing 2.5 mmol of alkene in pentane was removed and added to pentane (5 ml) in a round-bottomed flask and cooled in an acetone/carbon dioxide cooling bath. A solution of epoxide in pentane was then prepared in the same way as the alkene solution. An aliquot containing 5.0 mmol of epoxide was removed and added to the reaction mixture. A solution of bromine (3.1 mmol) in pentane (2.5 ml) was placed in a dropping funnel and added to the stirred reaction mixture portionwise over 1 hour. The resulting orange solution was allowed to warm to room temperature and then washed, first with sodium thiosulphate solution (2%, 25 ml) and then with water (distilled, 3 x 50 ml). The aqueous phases were backwashed with pentane (10 ml). The combined organic phases were dried over magnesium sulphate, filtered and then concentrated *in vacuo* to leave the crude products, a mixture of β,β'-dibromoether(s) and dibromide which was analysed by ^{1}H n.m.r. spectroscopy. Chromatography on silica using 40-60 petroleum ether:dichloromethane (3:1) as eluent, and distillation *in vacuo* furnished β,β'-dibromother(s) as a clear, colourless liquid.

Method C

This method was used when either the alkene or epoxide was a liquid but the other one was a gas at room temperature and pressure.

The appropriate amount of the liquid reagent was stirred with pentane (5 ml) in an

acetone/carbon dioxide cooling bath. A 10 ml measuring cylinder with a ground-glass stopper was sealed with a rubber septum and cooled in a acetone/carbon dioxide cooling bath. A measured volume of the gaseous reagent was then condensed into the measuring cylinder. Pentane was added to the condensed reagent using a syringe. An aliquot containing the required amount of reagent in pentane was removed and added to the cooled reaction mixture. A solution of bromine (3.1 mmol) in pentane (2.5 ml) was placed in a dropping funnel and added to the stirred reaction portionwise over 1 hour. The resulting orange solution was allowed to warm to room temperature and then washed, first with sodium thiosulphate solution (2%, 25 ml) and then with water (distilled, 3 x 50 ml). The aqueous phases were backwashed with pentane (10 ml). The combined organic phases were dried over magnesium sulphate, filtered, and concentrated *in vacuo* to leave the crude products, a mixture of β,β'-dibromoether(s) and dibromide which was analysed by ^{1}H n.m.r. spectroscopy. Chromatography on silica using 40-60 petroleum ether:dichloromethane (3:1) as eluent, and distillation *in vacuo* furnished β,β'-dibromoether(s) as a clear, colourless liquid.

2,3-Dimethylbut-2-ene (XXXIX) and ethylene oxide (XVIII)

The reaction was carried out *via* Method A to produce a mixture of β,β'-dibromoether (XL) and dibromide (IV) in a ratio of 67:33. Purification allowed the isolation of β, β'-dibromoether (XL) as a clear, colourless liquid in 38% yield, b.p. 175-178 °C (dec.) at 758.4 mmHg^{-1}, (found: C, 33.86; H, 5.63. $C_8H_{16}Br_2O$ requires C, 33.36; H, 5.60%); δ_H (400 MHz; $CDCl_3$) 1.38 (6H, s, -C(CH_3)$_2$O-), 1.78 (6H, s, BrC(CH_3)$_2$-), 3.38 (2H, t, *J* 6.2 Hz, OCH_2-) and 3.71 (2H, t, *J* 6.2 Hz, -CH_2Br); δ_C (100.6 MHz, $CDCl_3$) 21.6 (-OC(CH_3)$_2$-), 29.9 (BrC(CH_3)$_2$-), 31.1 (BrCH_2-), 63.3 (-OCH_2CH_2Br), 73.1 (BrC(CH_3)$_2$-), and 79.9 (-OC(CH_3)$_2$); *m/z* (C.I.) 308 (12%), 306 (28%) and 304 (13%) [$(M+NH_4)^+$ 1:2:1 isotope pattern for compound containing Br_2], and 165 (73%) and 163 (100%) [$(CH_3)_2C)_2Br^+$].

cis-But-2-ene (VI) and propylene oxide (XLII)

The reaction was carried out *via* Method C to produce a mixture of β,β'-dibromoethers and dibromide (XLVI) in a raito of 85:15. The mixture was not separated. β,β'-Dibromoethers: δ_H (220 MHz; $CDCl_3$) 1.27 (m, -OCC<u>H</u>$_3$), 1.65 (m, BrCC<u>H</u>$_3$), 3.20-3.79 (broad m, OC<u>H</u>), and 4.10 (m, BrC<u>H</u>). Dibromide (XLVI): δ_H (220 MHz; $CDCl_3$) 1.78 (6H, d, *J* 6 Hz, 2 x -CHC<u>H</u>$_3$), and 4.45 (2H, m, 2 x -C<u>H</u>CH$_3$).

cis-But-2-ene (VI) and 2-methyl-but-2-ene oxide (XLIII)

The reaction was carried out *via* Method C to produce a mixture to β,β'-dibromoethers and dibromide (XLVI) in a ratio of 38:62. The mixture was not separated. β,β'-Dibromoethers: δ_H (220 MHz; $CDCl_3$) 1.25 (m, -OCC<u>H</u>$_3$), 1.70 (m, BrCC<u>H</u>$_3$), 3.55-3.81 (broad m, -OC<u>H</u>), and 4.03-4.25 (broad m, BrC<u>H</u>). Dibromide (XLVI): δ_H (220 MHz; $CDCl_3$) 1.78 (6H, d, *J* 6 Hz, 2 x -CHC<u>H</u>$_3$) and 4.45 (2H, m, 2 x -C<u>H</u>CH$_3$).

cis-But-2-ene (VI) and 2,3-dimethylbut-2-ene oxide (XLIV)

The reaction was carried out *via* Method C to produce a mixture of β,β'-dibromoethers and dibromide (XLVI) in a ratio of 5:95. The mixture was not separated. β,β'-Dibromoethers: δ_H (220 MHz; $CDCl_3$) 1.21-1.63 (broad m, CC<u>H</u>$_3$) and 4.05-4.20 (m, C<u>H</u>). Dibromide (XLVI): δ_H (220 MHz; $CDCl_3$) 1.77 (6H, d, *J* 6.5 Hz, 2 x -CHC<u>H</u>$_3$) and 4.43 (2H, m, 2 x -C<u>H</u>CH$_3$).

trans-But-2-ene (VII) and propylene oxide (XLII)

The reaction was carried out *via* Method C to produce a mixture of β,β'-dibromoethers and dibromide (XLVII) in a ratio of 64:36. The mixture was not separated. β,β'-Dibromoethers: δ_H (220 MHz; $CDCl_3$) 1.27 (m, $BrCC\underline{H}_3$), 1.68 (m, $-OCC\underline{H}_3$) and 3.18-4.10 (broad m, -C<u>H</u>). Dibromide (XLVII): δ_H (220 MHz; $CDCl_3$) 1.89 (6H, d, *J* 6 Hz) and 4.15 (2H, m, 2 x $C\underline{H}CH_3$).

trans-But-2-ene (VII) and 2-methylbut-2-ene oxide (XLIV)

The reaction was carried out *via* Method C to produce a mixture of β,β'-dibromoethers and dibromide (XLVII) in a ratio of 30:70. The mixture was not separated. β,β'-Dibromoethers: δ_H (220 MHz; $CDCl_3$) 1.20-1.32 (broad m, $-OCC\underline{H}_3$), 1.62-1.75 (broad m, $BrCC\underline{H}_3$), 3.55-3.70 (broad m, -O<u>CH</u>) and 3.95-4.10 (broad m, Br<u>CH</u>). Dibromide (XLVII): δ_H (220 MHz; $CDCl_3$) 1.90 (6H, d, *J* 6 Hz, 2 x $-CHC\underline{H}_3$) and 4.13 (2H, m, 2 x $-C\underline{H}CH_3$).

trans-But-2-ene (VII) and 2,3-dimethylbut-2-ene oxide (XLIV)

The reaction was carried out *via* Method C to produce a mixture of β,β'-dibromoethers and dibromide (XLVII) in a ratio of 5:95. The mixture was not separated. β,β'-Dibromoethers: δ_H (220 MHz; $CDCl_3$) 1.25 (3H, m, $-OCHC\underline{H}_3$), 1.42 (6H, d, *J* 5 Hz, $-OCC\underline{H}_3$), 1.66 (3H, d, *J* 5 Hz, $BrCHC\underline{H}_3$), 1.83 (6H, d, *J* 5 Hz, $BrCC\underline{H}_3$), 3.70 (1H, m, -O<u>CH</u>) and 3.98 (1H, m, Br<u>CH</u>). Dibromide: δ_H (220 MHz; $CDCl_3$) 1.92 (6H, d, *J* 6 Hz, 2 x $-CHC\underline{H}_3$), and 4.15 (2H, m, 2 x $-C\underline{H}CH_3$).

2,3-Dimethylbut-2-ene (XXXIX) and propylene oxide (XLII)

The reaction was carried out *via* Method A to produce a mixture of β,β'-dibromoethers and dibromide (IV) in a ratio of 72:28. The mixture was not separated. β,β'-Dibromoethers: δ_H (220 MHz; $CDCl_3$) 1.28 (3H, d, *J* 6 Hz, -OCH(C$\underline{H}_3$), 1.40 (6H, s, -OC(C$\underline{H}_3$)$_2$-), 1.42 (6H, s, -OC(C$\underline{H}_3$)$_2$-), 1.70 (3H, d, *J* 6Hz, BrCH(C$\underline{H}_3$)-), 1.79 (6H, s, BrC(C$\underline{H}_3$)$_2$-), 1.81 (6H, s, BrC(C$\underline{H}_3$)$_2$-), 3.10 (1H, dd, *J* 7 and 7 Hz, -OC$\underline{H}_2$-), 3.25 (1H, dd, *J* 5 and 5 Hz, BrC$\underline{H}_2$-), 3.41 (1H, dd, *J* 7 and 7 Hz, -OC$\underline{H}_2$-), 3.59 (1H, dd, *J* 5 and 5 Hz, BrC$\underline{H}_2$-), 3.82 (1H, tq, *J* 5 and 6 Hz, -OC$\underline{H}$(CH$_3$)-), and 3.97 (1H, tq, *J* 7 and 6 Hz, BrC$\underline{H}$(CH$_3$)-). Dibromide (IV): δ_H (220 MHz; $CDCl_3$) 1.99 (12H, s, 4 x C$\underline{H}_3$).

2-Methylbut-2-ene (XLI) and ethylene oxide (XVIII)

The reaction was carried out *via* Method C to produce a mixture of β,β'-dibromoether and dibromide in a ratio of 85:15. Distillation *in vacuo* furnished β,β'-dibromoether as a clear, colourless liquid in 42% yield, b.p. 55-57 °C at 0.05 mm Hg^{-1}; δ_H (400 MHz; $CDCl_3$) 1.29 (3H, s, -O(C$\underline{H}_3$)$_2$-), 1.34 (3H, s, -OC(C$\underline{H}_3$)$_2$-), 1.68 (3H, d, *J* 6.8 Hz, BrCH(C$\underline{H}_3$)-), 3.37 (2H, t, *J* 6.6 Hz, Br-C$\underline{H}_2$-), 3.65 (1H, dt, *J* 9.5 and 6.6 Hz, -OC$\underline{H}_2$-), 4.07 (1H, q, *J* 6.8 Hz, BrC$\underline{H}$(CH$_3$)-); δ_C (100.6 MHz; $CDCl_3$) 21.0 (-OC(C$\underline{H}_3$)$_2$-), 21.3 (-OC(C$\underline{H}_3$)$_2$-), 24.0 (BrCH(C$\underline{H}_3$)-), 30.5 (BrC$\underline{H}_2$-), 56.3 (BrC$\underline{H}$(CH$_3$)), 62.7 (-OC$\underline{H}_2$-) and 77.8 (-OC(CH$_3$)$_2$-).

2-Methylbut-2-ene (XLI) and propylene oxide (XLII)

The reaction was carried out *via* Method A to produce a mixture of β,β'-dibromoethers and dibromide in a ratio of 85:15. The mixture was not separated. β,β'-Dibromoethers: δ_H (220 MHz; $CDCl_3$) 1.32-1.45 (m, -OCC$\underline{H}_3$), 1.68 (d, *J* 7 Hz, BrCC$\underline{H}_3$) and 3.05-4.02 (broad m, -OC$\underline{H}$ and BrC$\underline{H}$-). Dibromide: δ_H (220 MHz; $CDCl_3$) 1.83 (3H, s, BrC(C$\underline{H}_3$)$_2$),

1.95 (3H, d, *J* 6 Hz, BrCH($C\underline{H}_3$)), 1.99 (3H, s, BrC($C\underline{H}_3$)$_2$) and 4.47 (1H, q, *J* 6 Hz, Br$C\underline{H}$(CH_3)).

2-Methylbut-2-ene (XLI) and *cis*-but-2-ene oxide (XX)

The reaction was carried out *via* Method A to produce a mixture of β,β'-dibromoethers and dibromide in a ratio of 56:44. The mixture was not separated. β,β'-Dibromoethers: δ_H (220 MHz; $CDCl_3$) 1.21-1.33 (m, -OCC$\underline{H}_3$), 1.60-1.68 (m, BrCC$\underline{H}_3$), 3.87-3.93 (m, -OC$\underline{H}$) and 3.95-4.08 (broad m, -OC$\underline{H}$ and Br$C\underline{H}$). Dibromide: δ_H (220 MHz; $CDCl_3$) 1.82 (3H, s, BrC($C\underline{H}_3$)$_2$), 1.95 (3H, d, *J* 6 Hz, BrCH($C\underline{H}_3$), 1.99 (3H, s, BrC($C\underline{H}_3$)$_2$) and 4.45 (1H, q, *J* 6 Hz, Br$C\underline{H}$(CH_3)).

2-Methylbut-2-ene (XLI) and *trans*-but-2-ene oxide (XXI)

The reaction was carried out *via* Method A to produce a mixture of β,β'-dibromoethers and dibromide in a ratio of 65:35. The mixture was not separated. β,β'-Dibromoethers: δ_H (220 MHz; $CDCl_3$) 1.23-1.38 (m, -OCC$\underline{H}_3$), 1.63-1.75 (m, BrCC$\underline{H}_3$) and 3.52-4.02 (broad m, -OC$\underline{H}$ and Br$C\underline{H}$-). Dibromide: δ_H (220 MHz; $CDCl_3$) 1.83 (3H, s, BrC($C\underline{H}_3$)$_2$-), 1.95 (3H, d, *J* 6 Hz, BrCH($C\underline{H}_3$)), 1.99 (3H, s, BrC($C\underline{H}_3$)$_2$) and 4.45 (1H, q, *J* 6 Hz, Br$C\underline{H}$(CH_3)).

2-Methylbut-2-ene (XLI) and 2-methylbut-2-ene oxide (XLIII)

The reaction was carried out *via* Method A to produce a mixture of β,β'-dibromoethers and dibromide in a ratio of 33:67. The mixture was not separated. β,β'-Dibromoethers: δ_H (220 MH_3; $CDCl_3$) 1.28-1.42 (m, -OCC$\underline{H}_3$), 1.75-1.88 (m, BrCC$\underline{H}_3$), 3.65-3.82 (m,

-OC<u>H</u>) and 3.95-4.05 (m, BrC<u>H</u>$_3$). Dibromide: δ_H (220 MHz; $CDCl_3$) 1.83 (3H, s, BrC(C<u>H</u>$_3$)$_2$)-), 1.95 (3H, d, *J* 6 Hz, BrCH(C<u>H</u>$_3$)-), 1.99 (3H, s, BrC(C<u>H</u>$_3$)$_2$-) and 4.43 (1H, q, *J* 6 Hz, BrC<u>H</u>(CH$_3$)-).

2-Methylbut-2-ene (XLI) and 2,3-dimethylbut-2-ene oxide (XLIV)

The reaction was carried out *via* Method A to produce a mixture of β,β'-dibromoether and dibromide in a ratio of 34:66. The mixture was not separated. Dibromoether: δ_H (220 MHz; $CDCl_3$) 1.32 (6H, s, -OC(C<u>H</u>$_3$)$_2$-), 1.45 (6H, s, -OC(C<u>H</u>$_3$)$_2$-), 1.52 (6H, s, BrC(C<u>H</u>$_3$)$_2$-), 1.70 (3H, d, *J* 6 Hz, BrCH(C<u>H</u>$_3$)-) and 3.95 (1H, q, *J* 6 Hz BrC<u>H</u>(CH$_3$)-). Dibromide: δ_H (220 MHz; $CDCl_3$) 1.82 (3H, s, BrC(C<u>H</u>$_3$)$_2$-), 1.93 (3H, d, *J* 6 Hz, BrCH(C<u>H</u>$_3$)-), 1.97 (3H, s, BrC(C<u>H</u>$_3$)$_2$-), and 4.44 (1H, q, *J* 6 Hz, BrC<u>H</u>(CH$_3$)-).

2,3-Dimethylbut-2-ene (XXXIX) and 2-methylbut-2-ene oxide (XLIII)

The reaction was carried out *via* Method A to produce a mixture of β,β'-dibromoethers and dibromide (IV) in a ratio of 25:75. The mixture was not separated. Dibromoethers: δ_H (220 MHz; $CDCl_3$) 1.32-1.40 (m, -OCC<u>H</u>$_3$), 1.65-1.80 (m, BrCC<u>H</u>$_3$), 3.45 (1H, q, *J* 6 Hz, -OC<u>H</u>(CH$_3$)) and 3.70 (1H, q, *J* 6 Hz, BrC<u>H</u>(CH$_3$). Dibromide (IV): δ_H (220 MHz; $CDCl_3$) 2.00 (12H, s, 4 x -C<u>H</u>$_3$).

2,3-Dimethylbut-2-ene (XXXIX) and 2,3-dimethylbut-2-ene oxide (XLIV)

The reaction was carried out *via* Method A to produce a mixture of β,β'-dibromoether and dibromide (IV) in a ratio of 27:73. The mixture was not separated. β,β'-Dibromoether: δ_H (220 MHz; $CDCl_3$) 1.53 (12H, s, 2 x -OC(C<u>H</u>$_3$)-) and 1.80 (12H, s, 2 x BrC(C<u>H</u>$_3$)-).

Dibromide: δ_H (220 MHz; $CDCl_3$) 2.01 (12H, s, 4 x -$C\underline{H}_3$).

cis-But-2-ene (VI) and ethylene oxide (XVIII)

The reaction was carried out *via* Method B to produce a mixture of β,β'-dibromoethers and dibromide (XLVI) in a ratio of 73:27. The ratio of the major β,β'-dibromoether to minor β,β'-dibromoethers was >95:5 (by 400 MHz ^1H n.m.r. spectroscopy). Chromatography and distillation *in vacuo* allowed the isolation of the major β,β'-dibromoether (XLVIII) as a clear, colourless liquid, b.p. 220-223 °C (dec.) at 758.4 mm Hg , in 58% yield, (found: C, 27.84; H, 4.75. $C_6H_{12}Br_2O$ requires C, 27.72; H, 4.65%); δ_H (400 MHz; $CDCl_3$) 1.22 (3H, d, *J* 6.3 Hz, -OCH($C\underline{H}_3$)-), 1.62 (3H, d, *J* 6.8 Hz, BrCH($C\underline{H}_3$)-), 3.41 (2H, t, *J* 6.2 Hz, Br$C\underline{H}_2$-), 3.56 (1H, dq, *J* 4.4 and 6.3 Hz, -OC$\underline{H}$(CH_3)-), 3.73 (1H, dt, *J* 10.8 and 6.2 Hz, -O$C\underline{H}_2$-), 3.82 (1H, dt, *J* 10.8 and 6.2 Hz, -O$C\underline{H}_2$-), and 4.11 (1H, dq, *J* 4.4 and 6.8 Hz, BrC$\underline{H}$(CH_3)-); δ_C (100.6 MHz; $CDCl_3$) 15.8 (-OCH($\underline{C}H_3$)-), 20.3 (BrCH($\underline{C}H_3$)-), 30.4 (Br$\underline{C}H_2$-), 51.4 (Br$\underline{C}$H(CH_3)-), 69.4 (-O$\underline{C}H_2$-), 79.1 (-OCH(CH_3)-); *m/z* (E.I.) 263 (1%), 261 (2%) and 259 (2%) [M+] 153 (93%) and 151 (94%) [$BrCH_2CH_2O^+$=$CHCH_3$], 137 (85%) and 135 (87%) [$(CH_3C)_2Br$+], 109 (99%) and 107 (100%) [$(H_2C)_2Br^+$ or H_3CCH=Br^+] and 95 (20%) and 93 (21%) [CH_2=Br^+].

trans-But-2-ene (VII) and ethylene oxide (XVIII)

The reaction was carried out *via* Method B to produce a mixture of β,β'-dibromoethers and dibromide (XLVII) in a ratio of 68:32. The ratio of the major β,β'-dibromoether to minor β,β'-dibromoethers was >95:5 (by 400 MHz ^1H n.m.r. spectroscopy). Chromatography and distillation *in vacuo* allowed the isolation of the major β,β'-dibromoether (IL) as a clear, colourless liquid, b.p. 236-239 °C (dec.) at 758.4 mm Hg , in 61% yield. ($C_6H_{12}Br_2O$ requires 259.9799. Found (M^+), 259.9791); δ_H (400

MHz; $CDCl_3$) 1.25 (3H, d, *J* 6.2 Hz, -OCH($C\underline{H}_3$)-), 1.66 (3H, d, *J* 6.8 Hz, BrCH($C\underline{H}_3$)-), 3.44 (2H, t, *J* 6.4 Hz, Br$C\underline{H}_2$-), 3.49 (1H, dq, *J* 4.8 and 6.2 Hz, -O$C\underline{H}$(CH_3)-), 3.80 (1H, dt, *J* 10.7 and 6.4 Hz, -O$C\underline{H}_2$-), 3.81 (1H, dt, *J* 10.7 and 6.4 Hz, -O$C\underline{H}_2$-), and 4.11 (1H, dq, *J* 4.8 and 6.8 Hz, Br$C\underline{H}$(CH_3)-). δ_C (100.6 MHz; $CDCl_3$) 17.1 (-OCH($\underline{C}H_3$)-), 21.4 (BrCH($\underline{C}H_3$)-), 30.4 (Br$\underline{C}H_2$-), 52.8 (Br$\underline{C}$H(CH_3)-), 69.5 (-O$\underline{C}H_2$-) and 79.7 (-O$\underline{C}$H(CH_3)-). *m/z* (E.I.) 263 (5%), 261 (9%) and 259 (5%) [M^+], 153 (99%) and 151 (100%) [$BrCH_2CH_2O^+$=$CHCH_3$], 137 (84%) and 135 (85%) [$(CH_3C)_2Br^+$] and 109 (91%) and 107 (91%) [$(H_3C)_2Br^+$ or H_3CCH=Br^+].

2,3-Dimethylbut-2-ene (XXXIX) and *cis*-but-2-ene oxide (XX)

The reaction was carried out *via* Method A to produce a mixture of β,β'-dibromoethers and dibromide (IV) in a ratio of 90:10. The ratio of the major β,β'-dibromoether to minor β,β'-dibromoethers was >95:5 (by 400 MHz ^1H n.m.r. spectroscopy). Chromatography and distillation *in vacuo* allowed the isolation of the major β,β'-dibromoether (L) as a clear, colourless liquid, b.p. 152-154 °C (dec.) at 744.6 mm Hg^{-1}, in 56% yield, (found: C, 37.90; H, 6.45. $C_{10}H_{20}Br_2O$ requires C, 38.00; H, 6.38%). δ_H (400 MHz; $CDCl_3$) 1.22 (3H, d, *J* 6.2 Hz, -OCH($C\underline{H}_3$)-), 1.33 (3H, s, -OC($C\underline{H}_3$)$_2$-), 1.35 (3H s, -OC($C\underline{H}_3$)$_2$-), 1.62 (3H, d, *J* 6.8 Hz, BrCH($C\underline{H}_3$)-), 1.77 (3H, s, BrC($C\underline{H}_3$)$_2$-), 1.78 (3H, s, BrC($C\underline{H}_3$)$_2$-), 3.90 (1H, dq, *J* 3.7 and 6.2 Hz, -O$C\underline{H}$(CH_3)-) and 4.07 (1H, dq, *J* 3.7 and 6.8 Hz, Br$C\underline{H}$(CH_3)-), δ_C (100.6 MHz; $CDCl_3$) 16.3 (-OCH($\underline{C}H_3$)-), 18.9 (BrCH($\underline{C}H_3$)-), 21.7 and 22.0 (-OC($\underline{C}H_3$)$_2$-), 29.6 and 29.7 (BrC($\underline{C}H_3$)$_2$-), 52.1 (Br$\underline{C}$H(CH_3)-), 70.1 (-O$\underline{C}$H(CH_3)-), 73.9 Br$\underline{C}$H(CH_3)$_2$-) and 80.2 (-O$\underline{C}$H(CH_3)$_2$-); *m/z* (E.I.) 319 (1%), 317 (2%) and 315 (1%) [M^+], 195 (8%) and 193 (8%) [$BrCH(CH_3)CH(CH_3)O^+$=$C(CH_3)_2$], 165 (48%) and 163 (48%) [$(CH_3)_2CBr^+$], 137 (42%) and 135 (43%) [$(CH_3C)_2Br^+$], 123 (3%) and 121 (4%) [$(CH_3)_2C$=Br^+] and 109 (6%) and 107 (7%) [CH_3CH=Br^+].

2,3 Dimethylbut-2-ene (XXXIX) and *trans*-but-2-ene oxide (XXI)

The reaction was carried out *via* Method A to produce a mixture of β,β'-dibromoethers and dibromide (IV) in a ratio of 43:57. the ratio of the major β,β'-dibromoether to minor β,β'-dibromoethers was >95:5 (by 400 MHz ^{1}H n.m.r. spectroscopy). Chromatography and distillation *in vacuo* allowed the isolation of β,β'-dibromoether (LI) as a clear, colourless liquid, b.p. 168-170 °C (dec.) at 770.8 mm Hg^{-1}, in 23% yield, ($C_{10}H_{20}Br_2O$ requires 316.0883. Found (M^+) 316.0879); δ_H (400 MHz; $CDCl_3$) 1.21 (3H, d, *J* 6.1 Hz, -OCH(C$\underline{H}_3$)-), 1.36 (3H, s, -OC(C$\underline{H}_3$)$_2$-), 1.37 (3H, s, -OC(C$\underline{H}_3$)$_2$-), 1.63 (3H, d, *J* 6.9 Hz, BrCH(C$\underline{H}_3$)-), 1.80 (3H, s, BrC(C$\underline{H}_3$)$_2$-), 1.81 (3H, s, BrC(C$\underline{H}_3$)$_2$-), 3.68 (1H, dq, *J* 4.4 and 6.1 Hz, -OC$\underline{H}$(CH$_3$)-) and 4.06 (1H, dq, *J* 4.4 and 6.9 Hz, BrC$\underline{H}$(CH$_3$)-); δ_C (100.6 MHz; $CDCl_3$) 19.7 (-OCH(C$\underline{H}_3$)-), 21.8 (BrCH(C$\underline{H}_3$)-), 21.8 and 22.6 (-OC(C$\underline{H}_3$)$_2$-), 29.7 and 29.8 (BrC(C$\underline{H}_3$)$_2$-), 55.8 (Br$\underline{C}$H(CH$_3$)-), 71.7 (-O$\underline{C}$H(CH$_3$)-), 74.4 Br$\underline{C}$(CH$_3$)$_2$-), and 80.2 (-O$\underline{C}$(CH$_3$)$_2$-); *m/z* (E.I.). 195 (11%) and 193 (11%) [BrCH(CH$_3$)CH(CH$_3$)O$^+$=C(CH$_3$)$_2$], 165 (36%) and 163 (36%) [(CH$_3$)$_2$C)$_2$Br$^+$], 137 (58%) and 135 (60%) [(CH$_3$CH)$_2$Br$^+$], 123 (3%) and 121 (3%) [(CH$_3$)$_2$C=Br$^+$], and 109 (7%) and 107 (7%) [CH$_3$CH=Br$^+$].

***cis*-But-2-ene (VI) and *cis*-but-2-ene oxide (XX)**

The reaction was carried out *via* Method C to produce a mixture of β,β'-dibromoethers and dibromide (XLVI) in a ratio of 59:41. The 400 MHz ^{1}H n.m.r. spectrum revealed there to be two major β,β'-dibromoethers in a ratio of 1:1, and the ratio of these major to minor β,β'-dibromoethers to be >95:5. Chromatography and distillation *in vacuo* allowed the isolation of the two major diastereoisomeric β,β'-dibromoethers (LII) and (LIII) in a 1:1 mixture as a clear, colourless liquid in 61% yield, δ_H (400 MHz; $CDCl_3$) 1.21 (2 x 3H, d, *J* 6.3 Hz) and 1.22 (2 x 3H, d, *J* 6.3 Hz) [2 x -OCH(C$\underline{H}_3$)-], 1.61 (2 x 3H, d, *J* 6.8 Hz) and 1.63 (2 x 3H, d, *J* 6.8 Hz) [2 x BrCH(C$\underline{H}_3$)-], 3.65 (2 x 1H, dq, *J* 4.3 and 6.3 Hz) and 3.67 (2 x 1H, dq, *J* 4.7 and 6.8 Hz) [2 x -OC$\underline{H}$(CH$_3$)-], and 4.08 (2 x 1H, dq, *J* 4.3 and 6.8

Hz) and 4.10 (2 x 1H, dq, *J* 4.7 and 6.8 Hz) [2 x BrC<u>H</u>(CH_3)-]; δ_C (100.6 MHz; $CDCl_3$) 15.9 and 16.2 (2 x -CH(<u>C</u>H_3)), 20.0 and 20.2 (2 x BrCH(<u>C</u>H_3)-), 51.4 and 51.7 (2 x Br<u>C</u>H(CH_3)-) and 77.2 and 77.3 (2 x -O<u>C</u>H(CH_3)-); *m/z* (E.I.) 291 (5%), 289 (9%) and 287 (5%) [M^+], 181 (86%) and 179 (86%) [$BrCH(CH_3)CH(CH_3)O^+{=}CHCH_3$], 137 (99%) and 135 (100%) [$(CH_3CH)_2Br^+$] and 109 (13%) and 107 (13%) [$CH_3CH{=}Br^+$].

trans-But-2-ene (VII) and _trans_-but-2-ene oxide (XXI)

The reaction was carried out *via* Method C to produce a mixture of β,β'-dibromoethers and dibromide (XLVII) in a ratio of 53:47. The 400 MHz ^1H n.m.r. spectrum revealed there to be two major β,β'-dibromoethers in a ratio of 1:1, and the ratio of these major to minor β,β'-dibromoethers to be >95.5. Chromatography and distillation *in vacuo* allowed the isolation of the two major diastereoisomeric β,β'-dibromoethers (LIV) and (LV) in a 1:1 mixture as a clear, colourless liquid in 47% yield, δ_H (400 MHz; $CDCl_3$) 1.22 (2 x 3H, d, *J* 6.2 Hz) and 1.25 (2 x 3H, d, *J* 6.2 Hz) [2 x -OCH(C<u>H</u>$_3$)-], 1.64 (2 x 3H, d, *J* 6.8 Hz) and 1.67 (2 x 3H, d, *J* 6.9 Hz) [2 x BrCH(C<u>H</u>$_3$)-], 3.57 (2 x 1H, dq, *J* 4.7 and 6.2 Hz) and 3.59 (2 x 1H, dq, *J* 4.7 and 6.2 Hz) [2 x -OC<u>H</u>(CH_3)-], and 4.06 (2 x 1H, dq, *J* 4.7 and 6.8 Hz) and 4.11 (2 x 1H, dq, *J* 4.7 and 6.9 Hz) [2 x BrC<u>H</u>(CH_3)-]; δ_C (100.6 MHz; $CDCl_3$) 17.5 and 18.1 (2 x -OCH(<u>C</u>H_3)-), 21.3 and 21.8 (2 x BrCH(<u>C</u>H_3)-), 53.5 and 53.6 (2 x Br<u>C</u>H(CH_3)) and 77.5 and 78.1 (2 x -O<u>C</u>H(CH_3)-), *m/z* (E.I.) 291 (1%), 289 (2%) and 287 (1%) [M^+], 181 (47%) and 179 (48%) [$BrCH(CH_3)CH(CH_3)O^+{=}CH(CH_3)$], 137 (98%) and 135 (100%) [$(CH_3CH)_2Br^+$], 109 (6%) and 107 (7%) [$CH_3CH{=}Br^+$].

cis-But-2-ene (VI) and _trans_-but-2-ene oxide (XXI).

The reaction was carried out *via* Method C to produce a mixture of β,β'-dibromoethers and dibromide (XLVI) in a ratio of 55:45. The 400 MHz ^1H n.m.r. spectrum revealed

there to be two major β,β'-dibromoethers in a ratio of 2:1, and the ratio of these major to minor β,β'-dibromoethers to be >95:5. Chromatography and distillation *in vacuo* allowed the isolation of the two major diastereoisomeric β,β'-dibromoethers (LVI) and (LVII) in a 2:1 mixture as a clear, colourless liquid in 47% yield, δ_H (400 MHz; $CDCl_3$) major diastereoisomer first: 1.26 (3H, d, *J* 6.4 Hz, -OCH(C$\underline{H}_3$)-) or 1.28 (3H, d, *J* 6.6 Hz, -OCH(C$\underline{H}_3$)-) and 1.24 (3H, d, *J* 6.2 Hz, -OCH(C$\underline{H}_3$)-) or 1.25 (3H, d, *J* 6.3 Hz, -OCH(C$\underline{H}_3$)), 1.65 (3H, d, *J* 6.6 Hz, BrCH(C$\underline{H}_3$)-) or 1.67 (3H, d, *J* 6.6 Hz, BrCH(C$\underline{H}_3$)-) and 1.66 (3H, d, *J* 6.8 Hz, BrCH(C$\underline{H}_3$)-) or 1.68 (3H, d, *J* 6.8 Hz, BrCH(C$\underline{H}_3$)-), 1.28 (3H, d, *J* 6.6 Hz, -OCH(C$\underline{H}_3$)-) or 1.26 (3H, d, *J* 6.4 Hz, -OCH(C$\underline{H}_3$)-) and 1.25 (3H, d, *J* 6.3 Hz, -OCH(C$\underline{H}_3$)-) or 1.24 (3H, d, *J* 6.2 Hz, -OCH(C$\underline{H}_3$)), and 1.67 (3H, d, *J* 6.6 Hz, BrCH(C$\underline{H}_3$)-) or 1.65 (3H, d, *J* 6.6 Hz, BrCH(C$\underline{H}_3$)-) and 1.68 (3H, d, *J* 6.8 Hz, BrCH(C$\underline{H}_3$)-) or 1.66 (3H, d, *J* 6.8 Hz, BrCH(C$\underline{H}_3$)-), 4.08 (1H, dq, *J* 4.9 and 6.8 Hz, BrC$\underline{H}$(CH$_3$)-) or 4.11 (1H, dq, *J* 4.4 and 6.8 Hz, BrC$\underline{H}$(CH$_3$)-) and 4.06 (1H, dq, *J* 4.3 and 6.8 Hz, BrC$\underline{H}$(CH$_3$)-) or 4.17 (1H, dq, *J* 4.1 and 6.8 Hz, Br(C$\underline{H}$(CH$_3$)-), 3.60 (1H, dq, *J* 4.9 and 6.2 Hz, -OC$\underline{H}$(CH$_3$)-) or 3.71 (1H, *J* 4.4 and 6.3 Hz, -OC$\underline{H}$(CH$_3$)-) and 3.58 (1H, dq, *J* 4.3 and 6.2 Hz, -OC$\underline{H}$(CH$_3$)-) or 3.69 (1H, dq, *J* 4.1 and 6.3 Hz, -OC$\underline{H}$(CH$_3$)-), 3.71 (1H, dq, *J* 4.4 and 6.3 Hz, -OC$\underline{H}$(CH$_3$)-) or 3.60 (1H, dq, *J* 4.9 and 6.2 Hz, -OC$\underline{H}$(CH$_3$)-), and 4.11 (1H, dq, *J* 4.4 and 6.8 Hz, BrC$\underline{H}$(CH$_3$)-) or 4.08 (1H, dq, *J* 4.9 and 6.8 Hz, BrC$\underline{H}$(CH$_3$)-); δ_C (100.6 MHz; $CDCl_3$) major diastereoisomer first: 15.7 and 16.0 (-OCH(C$\underline{H}_3$)-), 17.7 and 18.0 (-OCH(C$\underline{H}_3$)-), 20.1 and 19.8 (BrCH(C$\underline{H}_3$)-), 21.4 and 21.1 (BrCH(C$\underline{H}_3$)-), 51.1 and 51.1 (BrC$\underline{H}$(CH$_3$)-), 51.8 and 53.3 (BrC$\underline{H}$(CH$_3$)-), 77.2 and 77.3 (-OC$\underline{H}$(CH$_3$)-) and 77.6 and 78.0 (-OC$\underline{H}$(CH$_3$)-); *m/z* (E.I.) 291 (3%), 189 (5%) and 187 (3%) [M^+, 181 (49%) and 179 (50%) [$BrCH(CH_3)CH(CH_3)O^+{=}CHCH_3$], 137 (29%) and 135 (29%) [$(CH_3CH)_2Br^+$], and 109 (1%) and 107 (1%) [$CH_3CH{=}Br^+$].

trans-But-2-ene (VII) and _cis_-but-2-ene oxide (XX).

The reaction was carried out *via* Method C to produce a mixture of β,β'-dibromoethers

and dibromide (XLVII) in a ratio of 69:31. The 400 MHz ^{1}H n.m.r. spectrum revealed there to be two major β,β'-dibromoethers in a ratio of 3:1 and the ratio of these major to minor β,β'-dibromoethers to be >95:5. Chromatography and distillation *in vacuo* allowed the isolation of the two major diastereoisomeric β,β'-dibromoethers (LVI) and (LVII) in a 1:3 mixture as a clear, colourless liquid in 57% yield, δ_H (400 MHz; $CDCl_3$) major diastereoisomer first: 1.24 (3H, d, *J* 6.2 Hz, -OCH(C$\underline{H}_3$)-) or 1.25 (3H, d, *J* 6.3 Hz, -OCH(C$\underline{H}_3$)-) and 1.26 (3H, d, *J* 6.4 Hz, -OCH(C$\underline{H}_3$)-) or 1.28 (3H, d, *J* 6.6 Hz, -OCH(C$\underline{H}_3$)-), 1.66 (3H, d, *J* 6.8 Hz, BrCH(C$\underline{H}_3$)-) or 1.68 (3H, d, *J* 6.8 Hz, BrCH(C$\underline{H}_3$)-) and 1.65 (3H, d, *J* 6.6 Hz, BrCH(C$\underline{H}_3$)-) or 1.67 (3H, d, *J* 6.6 Hz, BrCH(C$\underline{H}_3$)-); 1.25 (3H, d, *J* 6.3 Hz, -OCH(C$\underline{H}_3$)-) or 1.24 (3H, d, *J* 6.2 Hz, -OCH(C$\underline{H}_3$)-) and 1.28 (3H, d, *J* 6.6 Hz, -OCH(C$\underline{H}_3$)-) or 1.26 (3H, d, *J* 6.4 Hz, -OCH(C$\underline{H}_3$)-), 1.66 (3H, d, *J* 6.8 Hz, BrCH(C$\underline{H}_3$)-) or 1.68 (3H, d, *J* 6.8 Hz, BrCH(C$\underline{H}_3$)-) and 1.67 (3H, d, *J* 6.6 Hz, BrCH(C$\underline{H}_3$)-) or 1.65 (3H, d, *J* 6.6 Hz, BrCH(C$\underline{H}_3$)-), 3.58 (1H, dq, *J* 4.3 and 6.2 Hz, -OC$\underline{H}$(CH$_3$)-) or 3.69 (1H, dq, *J* 4.1 and 6.3 Hz, -OC$\underline{H}$(CH$_3$)-) and 3.60 (1H, dq, *J* 4.9 and 6.2 Hz, -OC$\underline{H}$(CH$_3$)-) or 3.71 (1H, dq, *J* 4.4 and 6.3 Hz, -OC$\underline{H}$(CH$_3$)-), 4.06 (1H, dq, *J* 4.3 and 6.8 Hz, BrC$\underline{H}$(CH$_3$)-) or 4.17 (1H, dq, *J* 4.1 and 6.8 Hz BrC$\underline{H}$(CH$_3$)-) and 4.08 (1H, dq, *J* 4.9 and 6.8 Hz, BrC$\underline{H}$(CH$_3$)-) or 4.11 (1H, dq, *J* 4.4 and 6.8 Hz, BrC$\underline{H}$(CH$_3$)-), 3.69 (1H, dq, *J* 4.1 and 6.3 Hz, -OC$\underline{H}$(CH$_3$)-) or 3.58 (1H, dq, *J* 4.3 and 6.2 Hz, -OC$\underline{H}$(CH$_3$)-) and 3.71 (1H, dq, *J* 4.4 and 6.3 Hz, -OC$\underline{H}$(CH$_3$)-) or 3.60 (1H, dq, *J* 4.9 and 6.2 Hz, -OC$\underline{H}$(CH$_3$)-), 4.17 (1H, dq, *J* 4.1 and 4.8 Hz, BrC$\underline{H}$(CH$_3$)-) or 4.06 (1H, dq, *J* 4.3 and 6.8 Hz, BrC$\underline{H}$(CH$_3$)-) and 4.11 (1H, dq, *J* 4.4 and 6.8 Hz, BrC$\underline{H}$(CH$_3$)-) or 4.08 (1H, dq, *J* 4.9 and 6.8 Hz, BrC$\underline{H}$(CH$_3$)-); δ_C (100.6 MHz; $CDCl_3$) major diastereoisomer first: 16.0 and 15.7 (-OCH(C$\underline{H}_3$)-), 18.0 and 17.7 (-OCH(C$\underline{H}_3$)-), 19.8 and 20.1 (BrCH(C$\underline{H}_3$)-), 21.1 and 21.4 (BrCH(C$\underline{H}_3$)-), 51.1 and 51.1 (BrC$\underline{H}$(CH$_3$)-), 53.3 and 51.8 (BrC$\underline{H}$(CH$_3$)-), 77.3 and 77.2 (-OC$\underline{H}$(CH$_3$)-) and 78.0 and 77.6 (-OC$\underline{H}$(CH$_3$)-); *m/z* (E.I.) 291 (1%), 289 (2%) and 287 (1%) [M^+], 181 (25%) and 179 (25%) [BrCH(CH$_3$)CH(CH$_3$)O$^+$=CHCH$_3$], 137 (16%) and 135 (16%) [(CH$_3$CH)$_2$Br$^+$], and 109 (1%) and 107 (1%) [CH$_3$CH=Br$^+$].

3-Bromobutan-2-ol (LIX).-

N-Bromosuccinimide (9.98 g, 56 mmol) was placed in a round-bottomed flask in an ice-water cooling bath. Ice (50 g) was added to the flask. *cis*-Butene (VI) (6.21 g, 111 mmol) was condensed into a septum-sealed measuring cylinder which was cooled in an acetone/carbon dioxide cooling bath. The *cis*-butene (VI) was added to the reaction mixture in one portion and stirred for 17 hours, by which time no solid succinimide remained. The clear solution was extracted with diethyl ether (2 x 30 ml) and the organic phases dried over magnesium sulphate. Filtration and concentration *in vacuo*, followed by distillation resulted in the isolation of the title compound (LIX) as a clear, colourless liquid (8.00 g, 93%), b.p. 153-154 °C; 758.6 mm Hg [lit.[28] 154 °C; 760 mm Hg]; $\upsilon_{max.}$ ($CHCl_3$) 3 446 (OH), 2 979 (CH) and 1 380 cm^{-1} (CH_3-C); δ_H (400 MHz; $CDCl_3$) 1.16 (3H, d, *J* 6.3 Hz, -CH(OH)C$\underline{H}_3$), 1.61 (3H, d, *J* 6.8 Hz, BrCH(C$\underline{H}_3$)-), 2.77 (1H, s, -OH, removed by D_2O shake), 3.62 (1H, dq, *J* 6.3 and 3.9 Hz, -C$\underline{H}$(OH)CH_3), and 3.99 (1H, dq, *J* 6.8 and 3.9 Hz, BrC$\underline{H}$(CH_3)-).

Bromination of 3-bromobutan-2-ol (LIX) and *trans*-but-2-ene (VII).-

The reaction was carried out *via* Method C to produce a mixture of 3-bromobutan-2-ol (LVIII) and dibromide (XLVII) as a pale yellow liquid in the ratio 45:55 (by 400 MHz ^1H n.m.r. spectroscopy). Distillation *in vacuo* furnished 3-bromobutan-2-ol (LIX) in 78% recovery as a clear, colourless liquid, b.p. 153-155 °C at 758.6 mm Hg [lit.[28] 154 °C at 760 mm Hg]; $\upsilon_{max.}$ ($CHCl_3$) 3 445 (OH), 2 979 (CH) and 1 380 cm^{-1} (CH_3-C); δ_H (400 MHz; $CDCl_3$) 1.15 (3H, d, *J* 6.3 Hz, -CH(OH)C$\underline{H}_3$), 1.61 (3H, d, *J* 6.8 Hz, BrCH(C$\underline{H}_3$)-), 2.77 (1H, s, -OH, removed by D_2O shake), 3.61 (1H, dq, *J* 6.3 and 3.9 Hz, -C$\underline{H}$(OH)(CH_3)) and 3.99 (1H, dq, *J* 6.8 and 3.9 Hz, BrC$\underline{H}$(CH_3)-).

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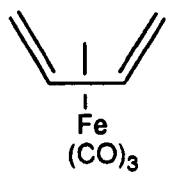
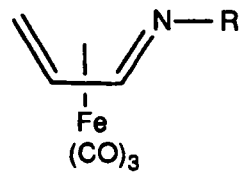
THE SYNTHESIS OF (1-AZADIENE)TRICARBONYLIRON(0) COMPLEXES

5. (1-AZADIENE)TRICARBONYLIRON(0) COMPLEXES

(Butadiene)tricarbonyliron(0) (*1*) was the first (diene)tricarbonyliron(0) complex to be synthesised[1]. Since its synthesis in 1930, many other (diene)tricarbonyliron(0) complexes have been prepared and they have been widely studied[2]. In contrast, (1-azadiene)tricarbonyliron(0)complexes (2) are less well known and have been much less extensively investigated. The majority of the work to date has consisted of structural and preparative studies and these are summarised in this introduction.



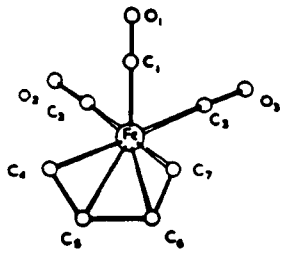
(*1*)

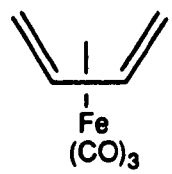


(*2*)

5.1 Structure of (1-Azadiene)tricarbonyliron(0) Complexes.-

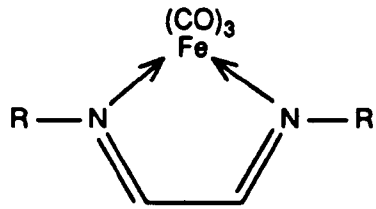
The general structure of (diene)tricarbonyliron(0) complexes was established by diffraction studies. For example, the structure of (butadiene)tricarbonyliron(0) (*1*) was first reported in 1960[3]. The carbon atoms of the diene unit are planar and the overall complex has square pyramidal geometry. The $Fe(CO)_3$ group does not have local C_{3v} symmetry since one C≡O group is unique while the other two are equivalent. The carbon-carbon bond lengths in the diene are approximately equal and the diene bonds with the metal in an "edge-on" fashion, with the carbon-carbon bonds perpendicular to the iron-carbon bonds. The π-orbitals of the ligand donate electron density to metal d-orbitals of the correct geometry for overlap. The empty π*-orbitals of the diene can then overlap with filled metal d-orbitals of the correct geometry and accept electron density in return. The electron accepting ability of the diene can be increased by the addition of electron withdrawing substituents.





(*1*)

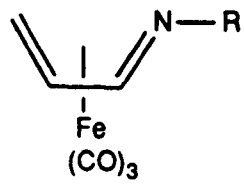
In contrast to (diene)tricarbonyliron(0) complexes there is no evidence for π-bonding in (1,4-diazadiene)tricarbonyliron(0) complexes (*3*). Coordination in these complexes takes place only through σ-bonding with the nitrogen lone pairs.



(*3*)

Consideration of structures (*1*) and (*3*) suggests that (1-azadiene)tricarbonyliron(0) complexes (*2*) could, in principle have two possible bonding modes:

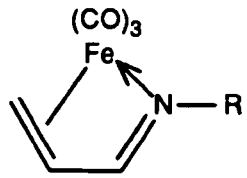
(i) Bonding mode A, in which there is η^4-coordination to the metal through the 1-azadiene.



Bonding mode A

(*2*)

(ii) Bonding mode B, in which the metal is bonded *via* η^2-coordination to the carbon-carbon double bond plus σ-bonding with the nitrogen lone pair.



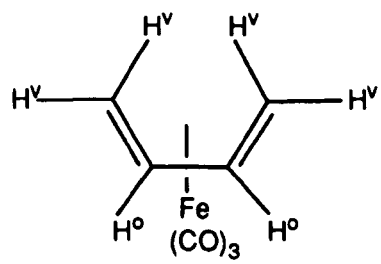
Bonding mode B

(*2*)

The majority of work on (1-azadiene)tricarbonyliron(0) complexes to date has been concerned with clarifying their bonding.

5.1.1 N.m.r. evidence.

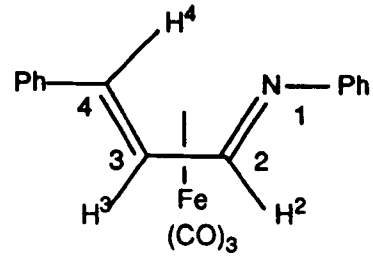
Early ^1H n.m.r. studies[4] suggested that the bonding in (1-azadiene)tricarbonyliron(0) complexes was similar to that in diene complexes. In (butadiene)tricarbonyliron(0) (*1*),



(*1*)

the terminal vinylidene protons (H^v) are shifted upfield (Δδ 4.7 and Δδ 3.4) compared to the free ligand (δ 5.11)[5]. The inner olefinic protons (H^o) in contrast are only slightly shifted upfield (Δδ 0.3) compared to the free ligand (δ 6.2)[5].

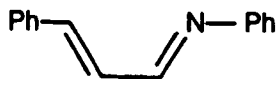
In a typical (1-azadiene)tricarbonyliron(0) complex (*4*), H^4 is considerably shifted upfield ($\Delta\delta$ 3.64-4.10), relative to the free ligand (δ 7.45)[4], whereas H^2 and H^3 are only shifted upfield slightly (about $\Delta\delta$ 0.8) relative to the free ligand (δ 8.10). This suggests that the bonding is similar to butadiene complex (*1*), *i.e.* bonding mode A is operating.



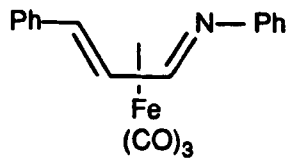
(*4*)

5.1.2 I.r. evidence.

The i.r. spectra of 1-azadienes, *e.g.* cinnamaldehydeanil (*5*), show two strong absorptions in the C=C and C=N regions. These absorptions move to lower frequencies on complexation (see Table 1, overleaf).



(*5*)



(*4*)

Compound	Absorption /cm^{-1}	
	C=N	C=C
(*5*)	1 621	1 571
(*4*)	1 475	1 429

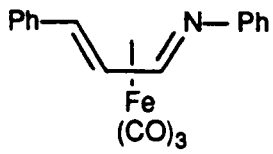
Table 1: I.r. absorptions for compounds (*4*) and (*5*)[4]

This change is due to a decrease in bond order and, hence, consistent with bonding mode A. Coordination *via* the lone pair, however, would be expected to cause a similar shift and so bonding mode B cannot be excluded on the basis of this evidence.

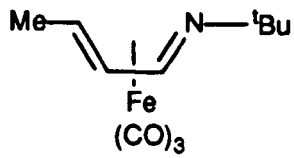
(1-Azadiene)tricarbonyliron(0) complexes (2) exhibit three strong C≡O bond absorptions in the 2 200-1 800 cm^{-1} region due to the $Fe(CO)_3$ moiety.

5.1.3 Photoelectron spectral studies.

He(I) and He(II) photoelectron spectra of complexes (*4*) and (*6*)[7] have been used to elucidate their electronic structure.



(*4*)



(*6*)

1-Azadiene complex (*6*), appeared to have both weakened π-bonding from the ligand to the metal and weakened π-backbonding from the metal to the ligand, compared to butadiene complex (*1*). This reduction in backbonding may be due to:

(i) asymmetry introduced into the ligand by the nitrogen atom, or

(ii) a bonding interaction between the nitrogen lone pair and the metal atom.

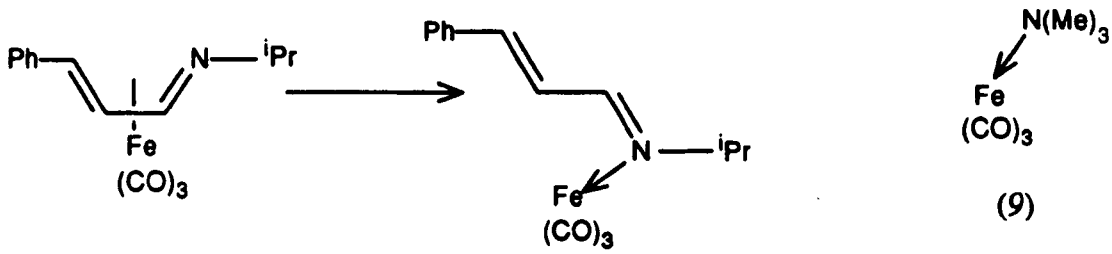
The consequence of the decreased π-backbonding and interaction with the nitrogen lone pair would be to increase electron density at the metal atom compared to the butadiene complex (*1*). This increased electron density results in a reduction in the ionisation energy of the 3n-bonding iron d-orbitals.

Photoelectron studies[7] also explain the greater stability of 1-azadiene complexes with phenyl substituents, such as complex (*4*). The electron density on the aromatic rings is increased on complexation. It seems likely, therefore, that the electrons donated to the ligand by the iron d-orbitals are delocalised from the 1-azadiene skeleton into the aromatic ring.

5.1.4 Matrix photolysis.

The potential involvement of the nitrogen atom in bonding was revealed by photochemical investigations of complexes in noble gas matrices[8]. On photolysis of the 1-azadiene complex (*7*) at 10 K in a methane matrix, a sixteen-electron σ-complex (*8*) was formed.

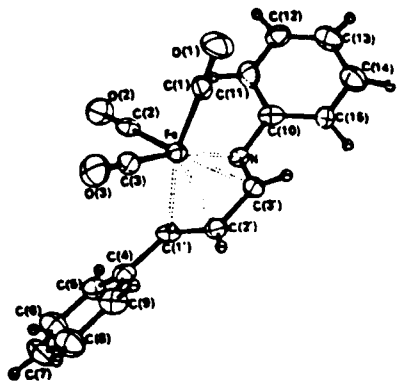
The structure of the product was confirmed by comparison of its i.r. spectrum with that of $Fe(CO)_3(NMe_3)$ (*9*), a sixteen-electron compound with a metal-nitrogen σ-bond.

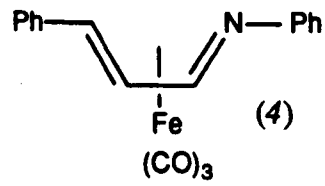


(*7*) (*8*) (*9*)

5.1.5 X-ray evidence.

Single crystal X-ray studies on complex (*4*)[9], reported in 1972, supported earlier suggestions that bonding was of mode A rather than mode B type, *i.e.* the nitrogen lone pair does not play an important role in the bonding of 1-azadienes with the tricarbonyliron(0) unit.





(*4*)

5.1.6 U.v. evidence.

Investigations have been carried out on a series of 4-phenyl substituted (1,4-diphenyl-1-azadiene)tricarbonyliron(0) complexes in cyclohexane solution[6]. Hydrocarbon polyenes have an intense absorption band due to a $\pi \rightarrow \pi^*$ transition, the wavelength and intensity of which increases with increasing length of the conjugated polyene chain. The introduction of a carbon-nitrogen double bond increases the wavelength and intensity of the transition in the same way as introducing an additional carbon-carbon double bond. Complexing a conjugated 1-azadiene system to the tricarbonyliron(0) moiety appears to have the same effect as reducing the number of double bonds by one, as demonstrated by the spectra of complexed and uncomplexed

N-4-chlorocinnamaldehydeanil (*10*) and (*11*), summarised in Table 2.

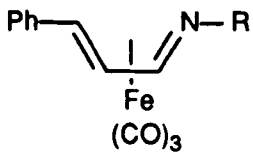
Compound	Absorption /nm (molar extinction coefficient /x10^{-3})
 R = 4-Cl-Ph- (*11*)	298 (29.7) 335 (18.5)
 R = 4-Cl-Ph- (*10*)	282 (21.9) 305 (17.0)

Table 2: U.v. spectral data for compounds (*10*) and (*11*)[6]

The resulting transitions are of increased energy either due to:

a. the change in conformation from transoid in the free ligand to cisoid in the complex, or

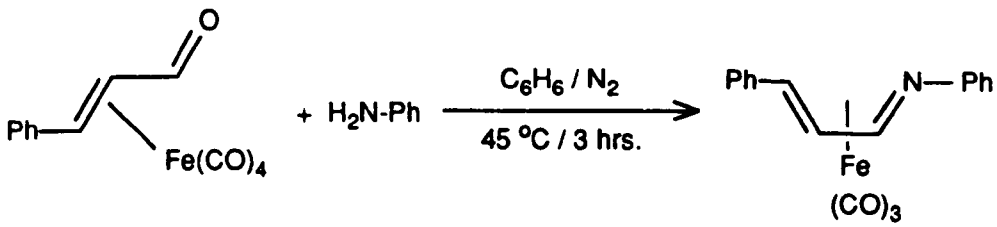
b. partial loss of conjugation on complexation.

4-Aryl substituents perturb the spectra of free ligands but have little effect on the spectra of complexes, suggesting an interruption of conjugative effects. This is consistent with the π,π-coordination in bonding mode A.

Overall, the evidence available strongly suggests that (1-azadiene)tricarbonyliron(0) complexes (2) have η^4-coordination through the diene unit, analogous to the bonding in (butadiene)tricarbonyliron(0) (*1*), *i.e.*bonding mode A is confirmed.

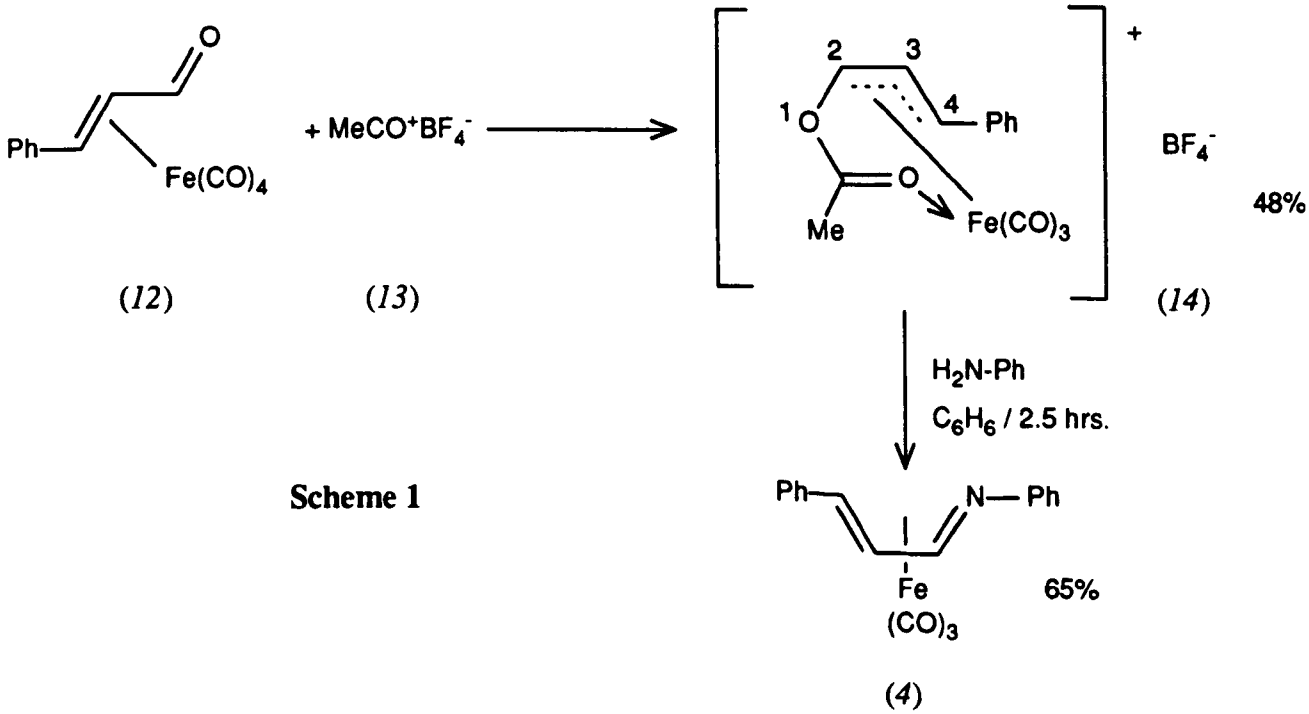
5.2 Preparation of (1-Azadiene)tricarbonyliron (0) Complexes.-

The first reported preparation of a (1-azadiene)tricarbonyliron (0) complex involved the condensation of aniline with (cinnamaldehyde)tetracarbonyliron(0) (*12*) as shown below[10].



(*12*) (*4*)

This conversion may also be achieved indirectly *via* the use of acetylium tetrafluoroborate (*13*) as an acylating agent (Scheme 1)[11]. Attack by aniline at C^2 of the cationic complex (*14*) leads to the 1-azadiene complex (*4*).

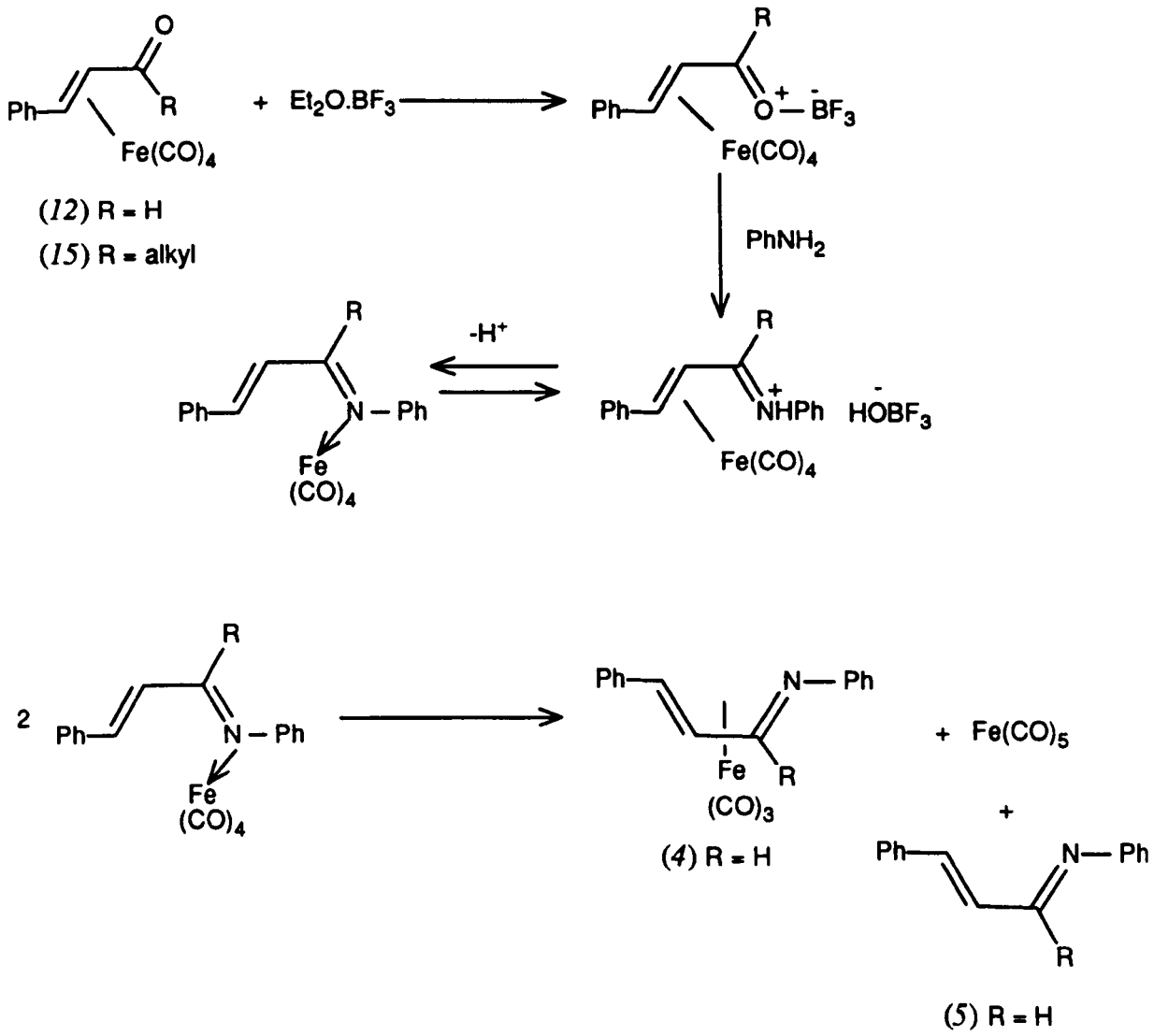


(*12*) (*13*) (*14*)

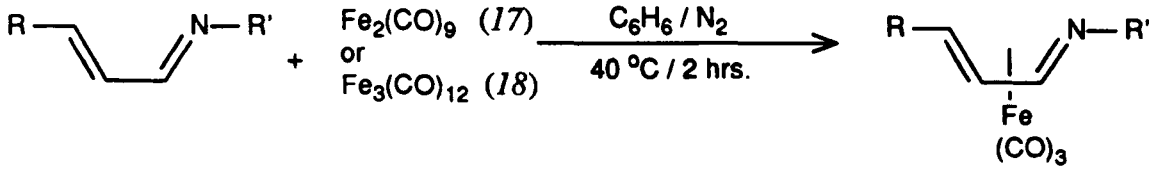
(*4*)

Scheme 1

Further work[12] led to the proposal that this type of reaction proceeded *via* a dissociative mechanism for tricarbonyliron(0) complex formation as outlined below for complex (*12*) and related ketone complexes (*15*)[13].



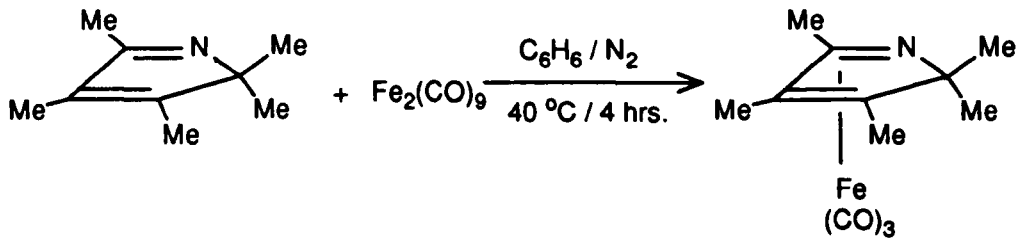
The first direct synthesis of (1-azadiene)tricarbonyliron(0) complexes was achieved by treatment of cinnamaldehydeanil (*5*) or crotonaldehyde-*n*-butylimine (*16*) with di-iron enneacarbonyl (*17*) or tri-iron dodecacarbonyl (*18*)[4]. This led to complexes (*4*) and (*19*) in rather low yield.



(*5*) R = R' = Ph
(*16*) R = Me, R' = ^{n}Bu

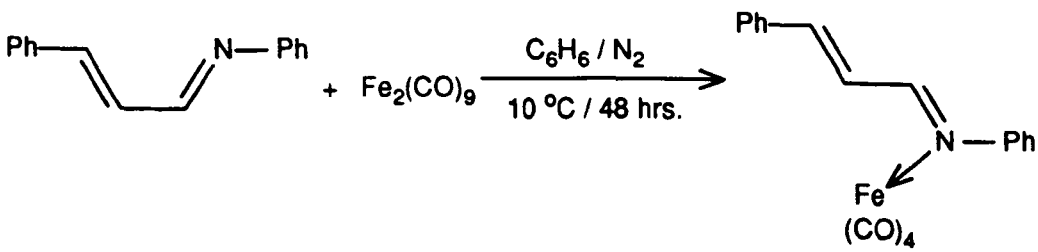
(*4*) R = R' = Ph, 29%
(*19*) R = Me, R' = ^{n}Bu, 10%

The same basic procedure may be used for a wide range of 1-azadienes, including the preparation of cyclic complexes. For example, the complex of cyclic imine (*20*) has been prepared in this way[14].



(*20*) (*17*)

Carrying out the complexation of cinnamaldehydeanil (*5*) at 10 °C led to the isolation of tetracarbonyl complex (*21*)[15].

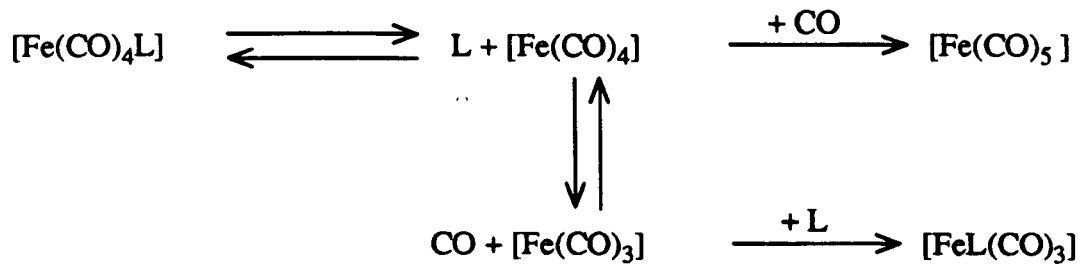


(*5*) (*17*) (*21*)

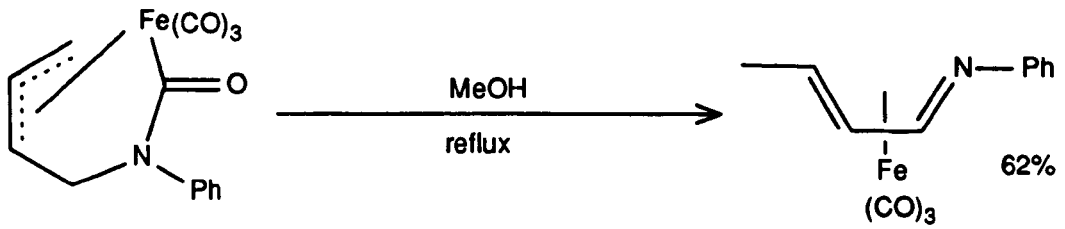
Scheme 2

It does seem feasible, therefore, that tetracarbonyl complexes are formed initially in complexation reactions but that these readily convert to the more stable tricarbonyl complexes.

The evidence currently available[16] suggests that the conversion occurs by further dissociation of the tetracarbonyl species as depicted in the following mechanism:

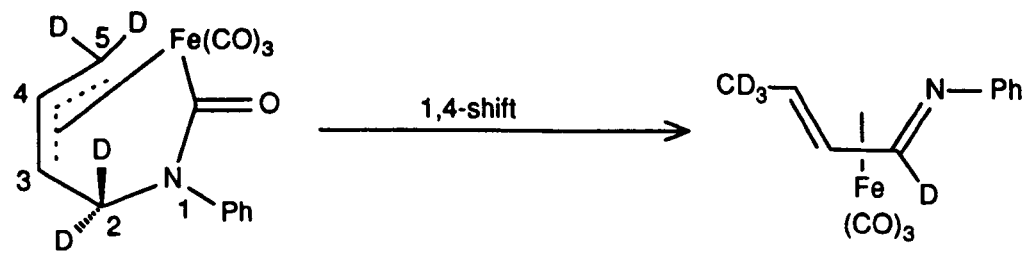


Finally, a 1-azadiene complex (*22*) has been prepared from the complexed lactam (*23*)[17].



(*23*) (*22*)

Studies using tetra-deuterio lactam (*24*) revealed that 1-azadiene complex (*22*) was formed *via* an intramolecular 1,4-shift of hydrogen from C^2 to C^5 (see Scheme 3).



(*24*)

Scheme 3

6. PREPARATION OF (CINNAMALDEHYDEANIL)-TRICARBONYLIRON(0)(*4*)

(Cinnamaldehydeanil)tricarbonyliron(0) (*4*) was chosen as a representative (1-azadiene)-tricarbonyliron(0) complex, suitable for use as a substrate in investigations of the reactivity of these complexes because:

(i) it is stable,

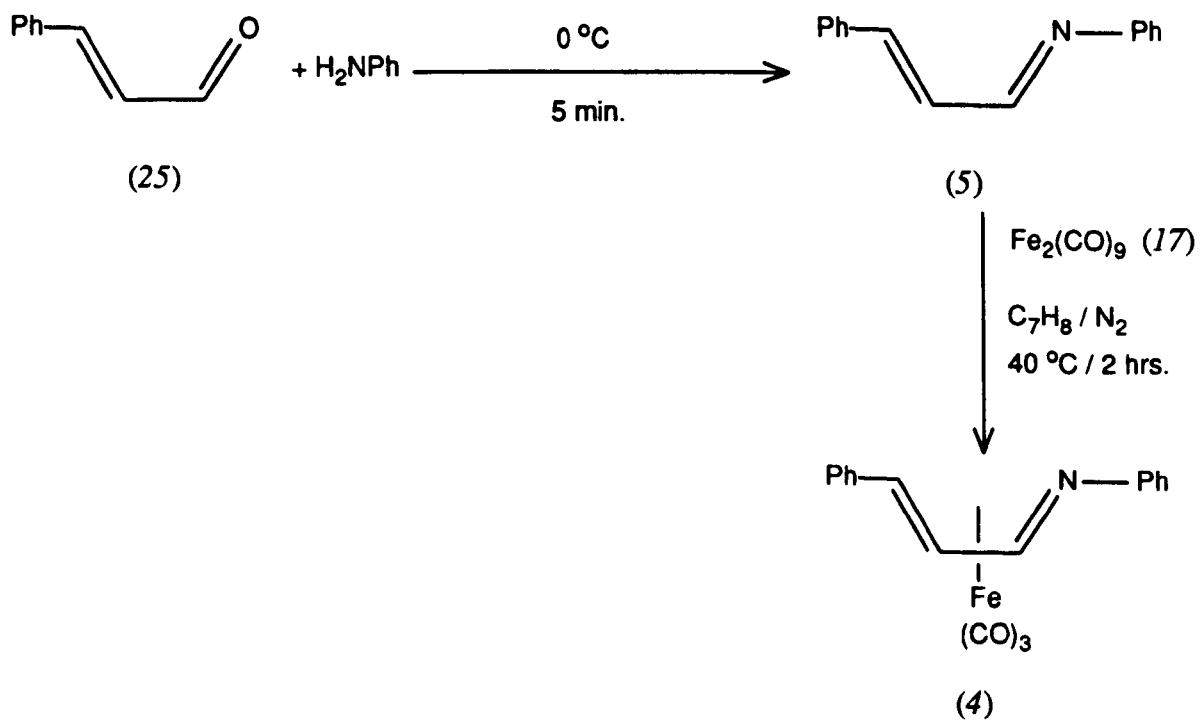
(ii) it is a crystalline solid (m.p. 108.5-109.5 °C [4]),

(iii) it has been fully characterised[4,6],

(iv) a simple, direct synthesis is available[4].

6.1 Thermal Complexation of Cinnamaldehydeanil (*5*).-

(Cinnamaldehydeanil)tricrabonyliron(0) (*4*) was one of the first (1-azadiene)-tricarbonyliron(0) complexes to be prepared[4]. Complexation involved the thermolysis of di-iron enneacarbonyl (*17*) with the easily prepared ligand cinnamaldehydeanil (*5*).



6.1.1 Preparation of starting materials.

Cinnamaldehydeanil (*5*) was prepared by the condensation of cinnamaldehyde (*25*) with aniline[15]. Aniline was added dropwise to the stirred aldehyde at 0 °C and this resulted in the immediate precipitation of a pale yellow solid. This solid was collected by filtration, dissolved in diethyl ether and dried over magnesium sulphate. Filtration and concentration left a solid which was crystallised from ethanol to furnish pale yellow crystals of anil (*5*) in 91% yield. The ^{1}H n.m.r. spectrum of this material contained a one-proton multiplet at δ 8.30 and a twelve-proton multiplet from δ 7.20 to δ 7.65, which agreed with the literature values[4]. Its i.r. spectrum was dominated by strong absorptions at 1 620 cm^{-1} (C=N) and at 1 570 cm^{-1} (C=C) which, together with the melting point and mass spectrum, was in good agreement with literature values[4].

Di-iron enneacarbonyl (*17*) was prepared by the photolysis of iron pentacarbonyl (*26*)[18]. Iron pentacarbonyl was diluted with acetic acid and irradiated with ultraviolet light for 7.5

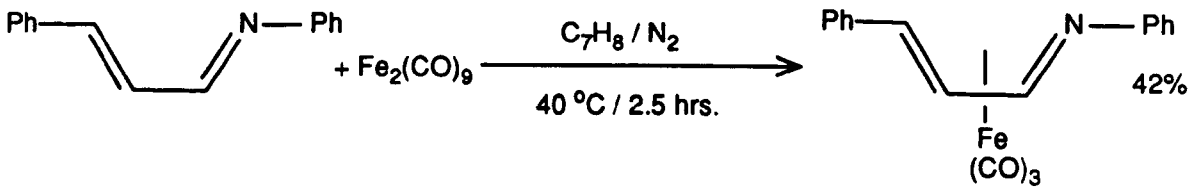
$$\underset{(26)}{2\ Fe(CO)_5} \xrightarrow[CH_3CO_2H\ /\ 7.5\ hrs.]{u.v.\ /\ N_2} \underset{(17)}{Fe_2(CO)_9} + CO$$

hours under a nitrogen atmosphere. The resulting orange crystals were collected by filtration and washed with ethanol and then diethyl ether. After drying under reduced pressure in the dark di-iron enneacarbonyl (*17*) was obtained as orange plate-like crystals in 48% yield. The i.r. spectrum of these crystals contained three strong C≡O absorptions at 2 085, 2 040 and 1 830 cm^{-1} which were in excellent agreement with literature values[19].

6.1.2 Complexation.

Complexation was then carried out using the standard 'direct synthesis' procedure[4]. Anil (*5*) and 1.1 mole-equivalents of di-iron enneacarbonyl (*17*) were heated to 40 °C in toluene under a nitrogen atmosphere for 2.5 hours. Filtration and concentration, followed by two recrystallisations from *n*-heptane furnished the tricarbonyliron complex (*4*) as ruby red needles in a yield of 42%. The ^{1}H n.m.r. spectrum of

complex (*4*) contained a one-protondoublet at δ 3.55 (Ph-C<u>H</u>=), a one-proton double doublet at δ 5.75 (Ph-CH=C<u>H</u>-), and an eleven-proton broad multiplet from δ 6.95 to δ 7.40 (2 x Ph-, and -N=C<u>H</u>-). Complexation was confirmed by the i.r. spectrum which was dominated by three sharp C≡O stretches between 2 050 and 1 950 cm^{-1}, and the mass spectrum which contained peaks at 347 (M^+, 27%) and 291 (M^+-2CO, 100%). All spectra were in good agreement with literature values[4].



(*5*) (*17*) (*4*)

The 'direct synthesis' method proved to be a straightforward and reliable complexation procedure. The yield, however, was constant at about 40% on range of scales from 0.2-2.0 g of starting anil (*5*). As it was intended to use complex (*4*) as a substrate to investigate the reactivity of (1-azadiene)tricarbonyliron(0) complexes, a procedure giving complex (*4*) in high yields would be less wasteful of resources in terms of both time and starting materials. With this in mind new approaches to the complexation of anil (*5*) were investigated.

6.2 Complexations Involving Ultrasound.-

6.2.1 Basic principles of ultrasound.

Several reviews of the basic principles of ultrasound are available[20]. Ultrasound is defined as sound of a frequency too high for the human ear to respond to[21]. The normal range of human hearing is between 16 Hz and 16 kHz and ultrasound is generally considered to be between 20 kHz and 500 MHz.

Ultrasound waves are like any sound wave and consist of alternating cycles of positive and negative pressure. The positive pressure compresses together the molecules of the liquid

or gas through which it is passing to create local areas of high density. This is the 'compression cycle'. A negative pressure then follows on and pulls the molecules apart again (and hence decreases the density of the molecules). This is the 'expansion cycle'. If the negative pressure in the liquid during the expansion cycle is greater than the attractive forces between the molecules then 'cavitation' will occur. Cavitation is the formation of gas bubbles, or cavities, in the liquid. The size of negative pressure necessary for cavitation to occur depends not just on the liquid but also its purity. Most liquids contain a certain number of small gas bubbles trapped within them. Ultrasound can cause these gas bubbles to oscillate and form cavities at lower pressures than those required to induce cavitation in a pure liquid[22].

Once cavities have formed, depending on their size they may:

(i) redissolve into the liquid if very small,

(ii) float away if very large, or

(iii) expand and contract in phase with the ultrasonic waves impinging upon them.

If the cavities are of the correct size to oscillate with the ultrasonic waves they will continue to grow. If the ultrasound is sufficiently intense the cavity may grow so quickly, and acquire such momentum, that succeeding compression waves cannot stop it growing. Once out of phase with the waves the bubbles are no longer stable. The internal pressure is not enough to support the size of the bubble and, helped by a compression wave, the bubble will implode.

The implosion compresses the vapour within the cavity and causes it to heat up. This compression occurs too quickly for the heat to transfer out into the surrounding liquid and very high temperatures (up to 5 000 °C) are generated very quickly in the localised area of the cavity. Cavitational collapse also serves to compress the contents of the cavity and generates localised high pressures of up to several hundred atmospheres. The whole collapse occurs very rapidly, thereby producing the high temperatures and pressures on a very small timescale (usually less than a microsecond).

The effects of this collapse can be felt in two distinct regions:

(i) within the cavity itself (in effect a high temperature, high pressure microreactor), and

(ii) in the immediate vicinity of the bubble where the shockwave produced will create enormous mechanical forces.

If ultrasound is applied to a heterogeneous reaction, such as one containing a solid-liquid interface, collapse of bubbles near the solid surface is asymmetric. A jet of liquid is generated which sweeps into the solid surface cleaning it and pitting it (hence exposing clean solid for reaction to take place at), and sweeping reacted species away. Cavitation in the liquid forms highly reactive species to attack the solid.

A detailed mathematical review of the physical aspects of ultrasound is available elsewhere[23].

6.2.2 Reactions utilising ultrasound.

Ultrasound irradiation produces localised 'hot spots' of high temperature and pressure which can cause reactions to go to completion in much shorter times. In addition, many reactions follow a different pathway to give different products depending on the source of energy provided for the reaction. For example, the effect of various energy sources on iron pentacarbonyl (*26*) is shown in Table 3 overleaf.

ENERGY SOURCE	MAIN PRODUCT
thermolysis	finely divided Fe powder
u.v. photolysis	$Fe_2(CO)_9$ (*17*)
i.r. photolysis	Fe atoms
sonication	$Fe_3(CO)_{12}$ (*18*)

Table 3: Reaction of $Fe(CO)_5$ (*26*) using different energy sources[20b]

Sonication of iron pentacarbonyl (*26*) was found to proceed *via* the following pathway:

$$\underset{(26)}{Fe(CO)_5} \xrightarrow[\text{alkane}]{)))} Fe(CO)_{5-n} + nCO \qquad (n = 1\text{-}5)$$

$$Fe(CO)_3 + \underset{(26)}{Fe(CO)_5} \longrightarrow Fe_2(CO)_8$$

$$Fe_2(CO)_8 + \underset{(26)}{Fe(CO)_5} \longrightarrow \underset{(18)}{Fe_3(CO)_{12}} + CO$$

In the presence of phosphines and phosphites substituted iron carbonyls were obtained, as follows:

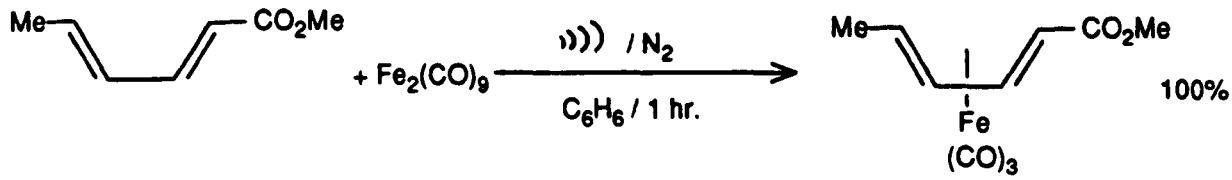
$$\underset{(26)}{Fe(CO)_5} + L \xrightarrow[\text{alkane}]{)))} Fe(CO)_4L + Fe(CO)_3L_2 + Fe(CO)_2L_3$$

L = phosphite/phosphine

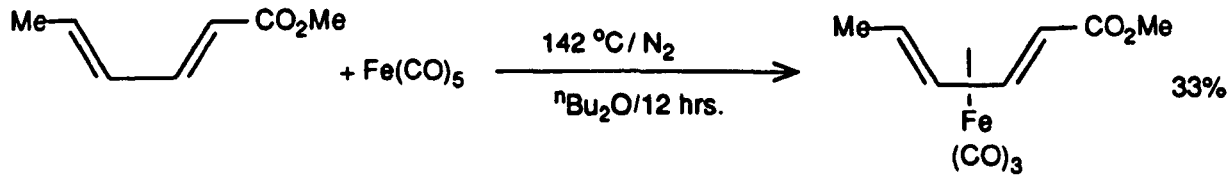
Studies on this system[24] indicated that as the volatility of the solvent was decreased, the intensity of cavitational collapse, the maximum temperature reached, and the rate of reaction all increased. The effect of increasing the solvent vapour pressure, therefore, was

to decrease the reaction rate.

The sonication of $Fe(CO)_5$ (*26*) results in the formation of the fourteen-electron species $Fe(CO)_3$. The $Fe(CO)_3$ moiety may then be trapped to give $Fe(CO)_3L_2$. It should therefore be possible to trap the $Fe(CO)_3$ with a diene. This reaction has indeed been reported for a series of substituted diene ligands using $Fe_2(CO)_9$ (*17*) as the source of $Fe(CO)_3$[25]. Reactions, such as the complexation of methyl sorbate (*27*), were found to proceed in much higher yields than any reported previously using thermal methods[26]:



(*27*) (*17*) (*28*)



(*27*) (*26*) (*28*)

6.2.3 Complexation of 1-azadienes using ultrasound.

The formation of (diene)tricarbonyliron(0) complexes from diene ligands can be achieved in high yield by the use of ultrasound. It was decided, therefore, to examine the complexation of 1-azadiene ligands *via* ultrasound in order to determine whether or not the resulting (1-azadiene)tricarbonyliron(0) complexes would be obtained in similarly high yields.

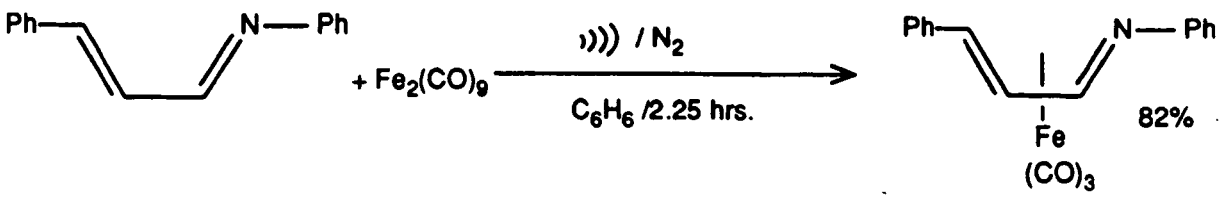
A commercially available ultrasound cleaning bath was filled with a measured volume of tap water containing about 5% (v/v) detergent. The reaction vessel was then supported in

the area of maximum cavitation in the centre of the bath. (Areas of maximum cavitation within the bath can be plotted by studying the pattern of holes punched in sheets of aluminium foil[27]). The reaction vessel was charged with cinnamaldehydeanil (*5*), 1.1 mole-equivalents of di-iron enneacarbonyl (*17*), and toluene, and the reaction mixture sonicated under a nitrogen atmosphere (agitation could be readily observed as small jets of solution spurted up against the walls of the vessel). After sonication for three hours, all solid di-iron enneacarbonyl (*17*) had disappeared and the temperature of the reaction mixture had increased from 21 to 44 °C. The resulting dark red solution was concentrated *in vacuo* to leave a dark red gum, which was chromatographed to give (cinnamaldehydeanil)tricarbonyliron(0) (*4*) as dark red needles in 55% yield. The ^{1}H n.m.r., i.r., and mass spectra, and the melting point of this material were identical to those obtained on complex (*4*) formed by thermal complexation.

Thus, sonication of cinnamaldehydeanil (*5*) and di-iron enneacarbonyl (*17*) gave a yield of 55%, a higher yield of complex (*4*) than obtained from the more conventional thermal method (41%). Investigations designed to optimise the conditions for the ultrasound reaction were then carried out. An initial attempt to improve yields by increasing reaction time from 3 to 6.75 hours furnished complex (*4*) in 58% yield, no significant improvement over the shorter reaction (55% yield).

The rate of ultrasound reactions has been found to be affected by the choice of solvent[24]. Cinnamaldehydeanil (*5*) and di-iron enneacarbonyl (*17*), were therefore subjected to ultrasound irradiation in a range of solvents. In each case the reaction was stopped when all solid di-iron enneacarbonyl (*17*) had disappeared. After concentration *in vacuo*, chromatography, and characterisation, the yields of complex (*4*) obtained were noted. As may be seen from Table 4, the best solvent of those examined proved to be benzene which gave an 82% yield of complex (*4*), a figure significantly higher than those obtained in other solvents.

In an attempt to optimise the reaction still further, the reaction in benzene was examined at several positions within the ultrasound bath. In each case the reaction vessel was adjusted to a position where visible cavitation occurred. Any position where cavitation could not be seen was ignored. The reaction was carried out in the centre of the ultrasound bath - 'position 1' (see Diagram 1), but with the bottom of the reaction vessel at a depth of 75 mm below the surface, rather than the depth of 25 mm previously used. Irradiation until all solid di-iron enneacarbonyl (*17*) had disappeared, followed by the usual work-up produced complex (*4*) in only 76% yield (see Table 5). The reaction vessel was returned to a depth of 25 mm and moved to the other locations of high cavitation within the bath. Reaction in these positions gave yields of complex (*4*) between 52% and 62%, a decrease from that obtained in 'position 1'. The best location for the reaction vessel within the ultrasound bath was its original central position at a depth of 25 mm.



(*5*) (*17*) (*4*)

SOLVENT	SOLVENT b.p./°C	REACTION TIME / hrs	MAXIMUM TEMP. / °C	YIELD OF COMPLEX (*4*) / %
Toluene	111	3	44	55
Cyclohexane	81	2.25	42.5	52
Xylenes	138-142	2.25	42	53
Petroleum Ether	60-80	2.25	39.5	52
Petroleum Ether	80-100	2.25	41	56
Diethyl Ether	35	2	35	62
THF	66	1.50	35	64
Benzene	80	2.25	40	82

Table 4: Variation of solvent for ultrasonic complexation of cinnamaldehydeanil (*5*)

DEPTH OF SCHLENK TUBE /mm	POSITION IN BATH (see Diag.1)	REACTION TIME /hrs.	MAXIMUM TEMP. /°C	YIELD OF COMPLEX (*4*) /%
25	1	2.25	40	82
75	1	2.50	39	76
25	2	3.25	29	55
25	3	2.25	34	62
25	4	2.25	40	52

Table 5: Variation of position of reaction vessel in ultrasound bath

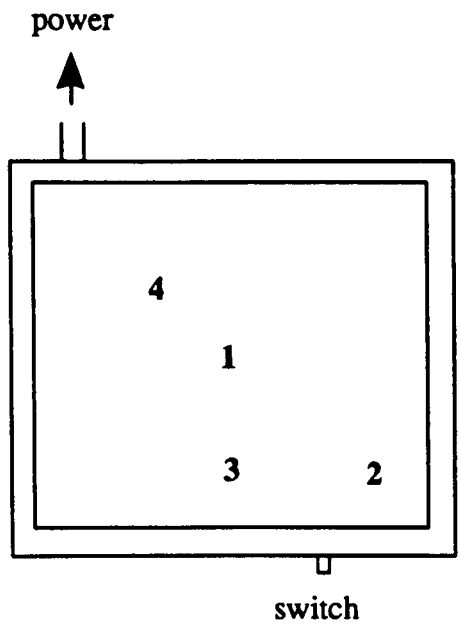


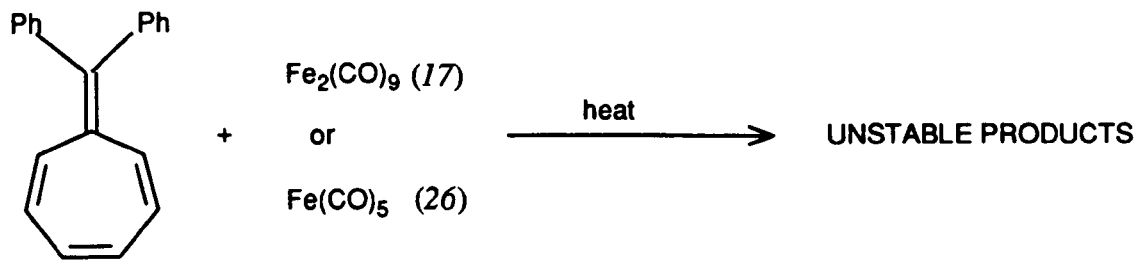
Diagram 1: Positions in the ultrasound bath

In conclusion, the complexation of cinnamaldehydeanil (*5*) in benzene using 1.1 mole-equivalents of di-iron enneacarbonyl (*17*) can be accomplished in high yields by the use of ultrasound irradiation. In favourable cases the yield of complex (*4*) obtained was very high (82%). The reaction, however, is not entirely reproducible (eight reactions [benzene/position 1/25 mm] gave yields of 55-82% with an average yield of 69%). The worst case, however, provided a higher yield of complex (*4*) than the standard thermal method (41%). Ultrasonic irradiation does provide, therefore, a more efficient complexation method for 1-azadienes than the standard thermal method.

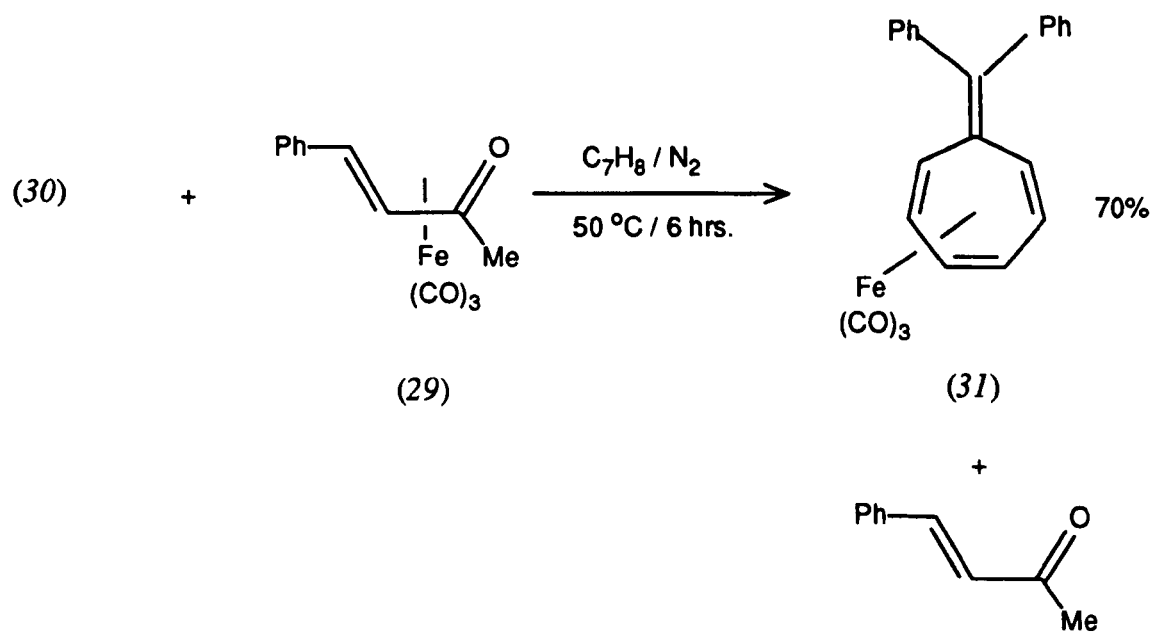
6.3 Complexations Involving Transfer Reactions.-

The synthesis of (diene)tricarbonyliron(0) complexes is usually carried out *via* reaction of the parent diene ligand with $Fe(CO)_5$ (*26*), $Fe_3(CO)_{12}$ (*18*), or $Fe_2(CO)_9$ (*17*). The first two of these processes require a long reaction time with high temperatures and produce only a low yield of complex. $Fe_2(CO)_9$ (*17*) requires a lower temperature and shorter reaction times but may give a mixture of products, especially if reacted with a polyene[28].

These problems may be overcome by using a (1-oxadiene)tricarbonyliron(0) complex, *e.g.* (benzylideneacetone)tricarbonyliron(0) (*29*), as a source of -$Fe(CO)_3$. The transfer of the -$Fe(CO)_3$ unit from the 1-oxadiene ligand to the diene takes place under mild conditions and can be particularly useful when complexation of the diene by 'direct' means is unsuccessful[29]. For example, 'direct' complexation of the conjugated polyene (*30*) using $Fe_2(CO)_9$ (*17*) or $Fe(CO)_5$ (*26*) as the source of -$Fe(CO)_3$ only results in the formation of unstable products, whereas a transfer reaction using (benzylideneacetone)-tricarbonyliron(0) (*29*) to supply -$Fe(CO)_3$ allows the isolation of the stable complex (*31*):



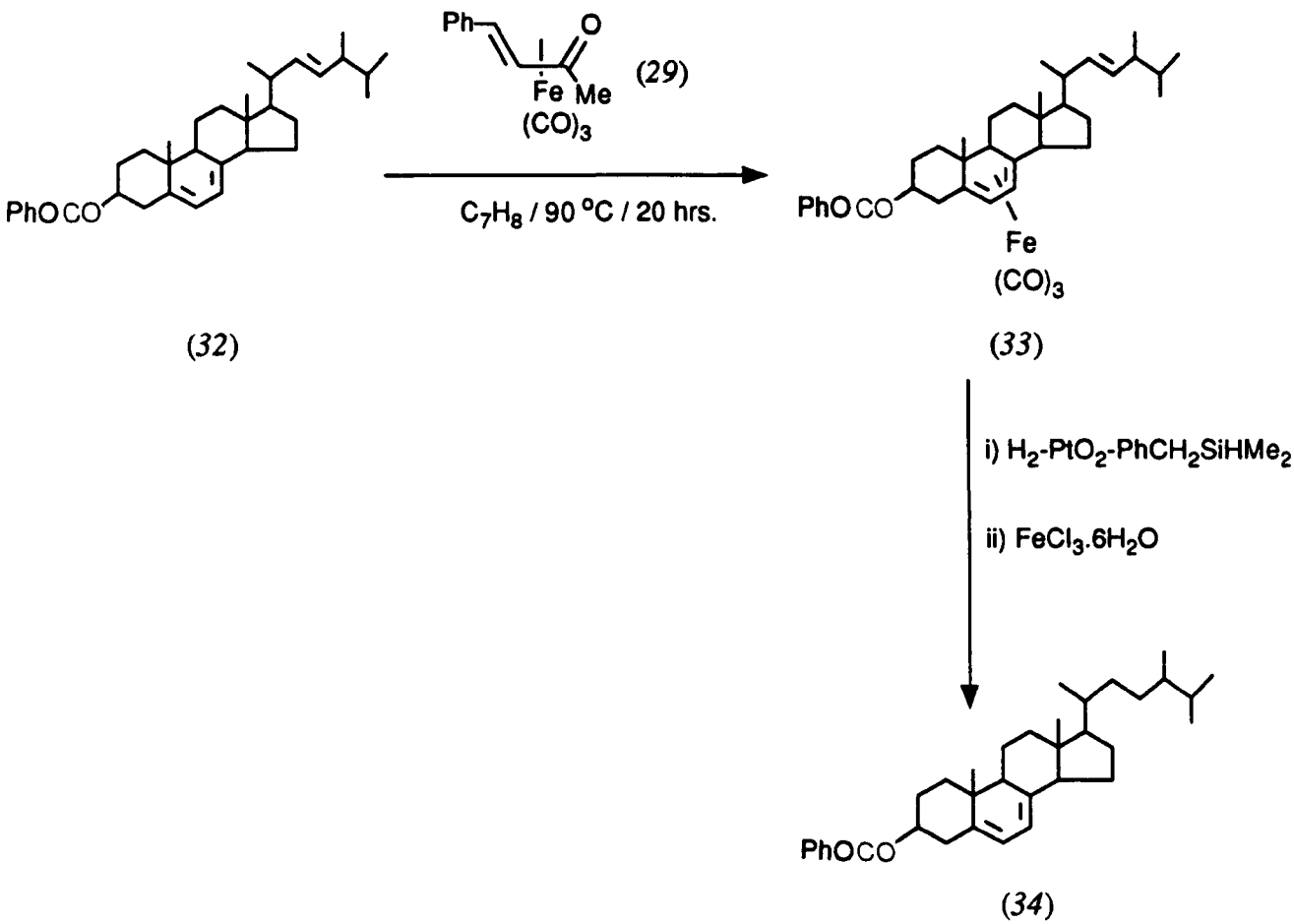
(*30*)



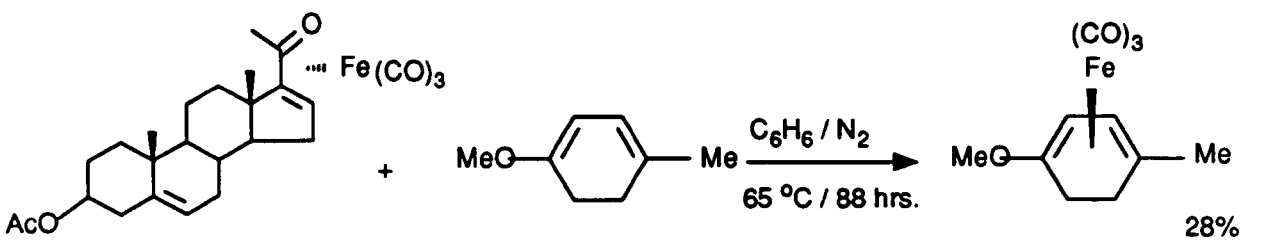
(*29*) (*31*)

(Benzylideneacetone)tricarbonyliron(0) (*29*) is an easily synthesised and readily available source of -$Fe(CO)_3$[28]. Further examples of its application in organic synthesis include its

use as a source of -$Fe(CO)_3$ in the protection of the B-ring diene system of ergosterol (*32*) to give steroid complex (*33*). The unprotected double bond in the side-chain can then be reduced without reducing the diene system. Subsequent removal of the -$Fe(CO)_3$ protecting group allows the isolation of 22,23-dihydroergosterol (*34*)[30].

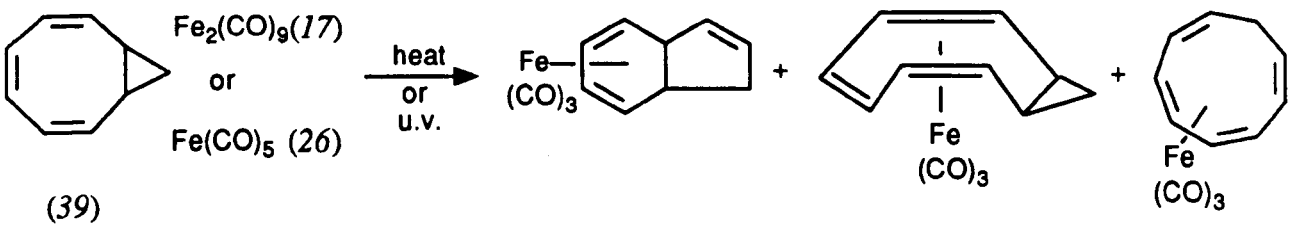


If an optically active oxadiene complex such as (*35*) is chosen as the source of -$Fe(CO)_3$ in a transfer reaction, then transfer of the tricarbonyliron(0) moiety to an unsymmetrical butadiene ligand, *e.g.* (*36*), produces an optically active diene complex (*37*)[31]:



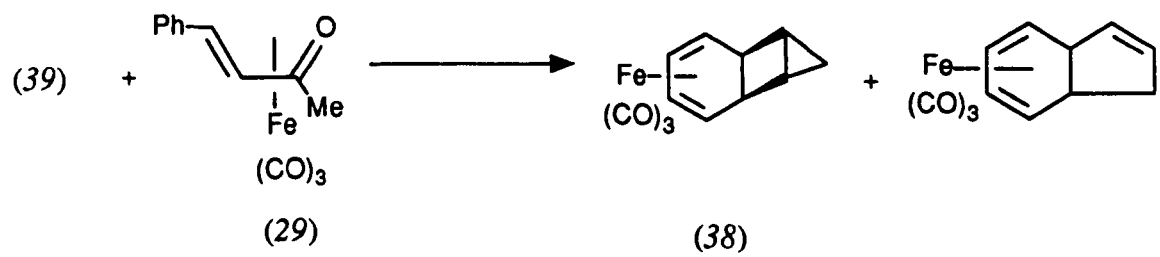
(*35*) (*36*) (*37*)

Transfer reactions from oxadiene complexes have also found a role in the trapping of diene-containing intermediates such as (*38*) which are formed in the course of a reaction but may have rearranged before they can be complexed by an iron carbonyl fragment generated thermally[32].



(*39*)

but



(*29*) (*38*)

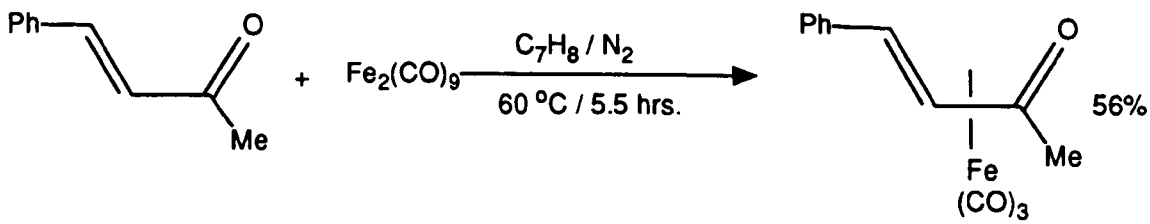
6.3.1 Transfer reactions to 1-azadienes.

No example of the transfer of -$Fe(CO)_3$ from an (oxadiene)tricarbonyliron(0) complex to a 1-azadiene ligand has been reported in the literature. It was decided, therefore, to examine

whether or not (1-oxadiene)tricarbonyiron(0) complexes would transfer the -$Fe(CO)_3$ unit to 1-azadienes and thus provide a novel approach to (1-azadiene)tricarbonyliron(0) complexes. As (benzylideneacetone)tricarbonyliron(0) (*29*) is the 1-oxadiene complex of choice in most examples of transfer of -$Fe(CO)_3$ to dienes, and cinnamaldehydeanil (*5*) was readily available, the feasibility of -$Fe(CO)_3$ transfer from a 1-oxadiene to a 1-azadiene was examined using these two compounds.

6.3.1.1 Preparation of (benzylideneacetone)tricarbonyliron(0) (*29*)

Benzylideneacetone (*40*) and di-iron enneacarbonyl (*17*) were stirred in toluene at 60 °C for 5.5 hours under a nitrogen atmosphere. The reaction mixture was filtered through alumina and concentrated *in vacuo* to leave a brown solid which was chromatographed and then recrystallised from hexane to give (benzylideneacetone)tricarbonyliron(0) (*29*) as orange crystals in 56% yield. These crystals had a melting point of 88-90 °C. The ^1H n.m.r. spectrum contained a three-proton singlet at δ 2.55 (-C<u>H</u>$_3$), one-proton doublets at δ 3.13 (Ph-C<u>H</u>=) and δ 6.08 (Ph-CH=C<u>H</u>-), and a five-proton multiplet from δ 7.30 - 7.40 (Ph-). Complexation was confirmed by the i.r. spectrum which contained peaks due to C≡O absorptions at 2 065, 2 005 and 1 985 cm^{-1}. All data were in good agreement with literature values[6,28].

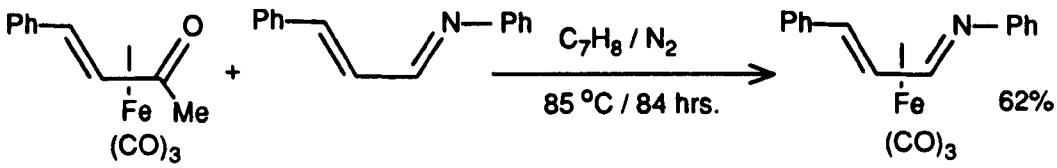


(*40*) (*17*) (*29*)

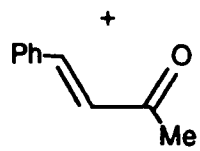
6.3.1.2 Transfer reaction to cinnamaldehydeanil (*5*)

The benzylideneacetone complex (*29*) and cinnamaldehydeanil (*5*) were suspended in toluene and stirred at 85 °C for 84 hours under a nitrogen atmosphere, after which time thin layer chromatography indicated that all starting complex (*29*) had been consumed.

The brown reaction mixture was allowed to cool and then filtered through alumina. Concentration *in vacuo* left an orange solid which was chromatographed to leave (cinnamaldehydeanil)tricarbonyliron(0) (*4*) as dark red needles in 62% yield. The melting point, and i.r., ^{1}H n.m.r., and mass spectra of these crystals were in good agreement with literature values[4].

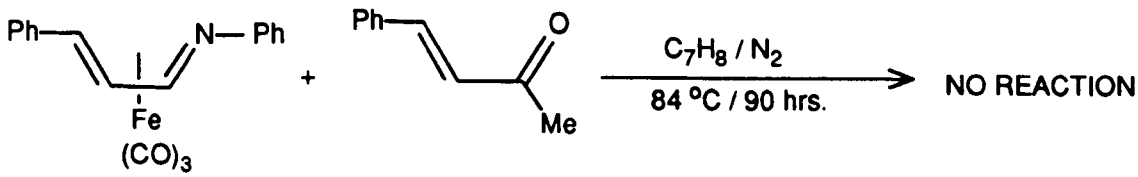


(*29*) (*5*) (*4*)



(*40*)

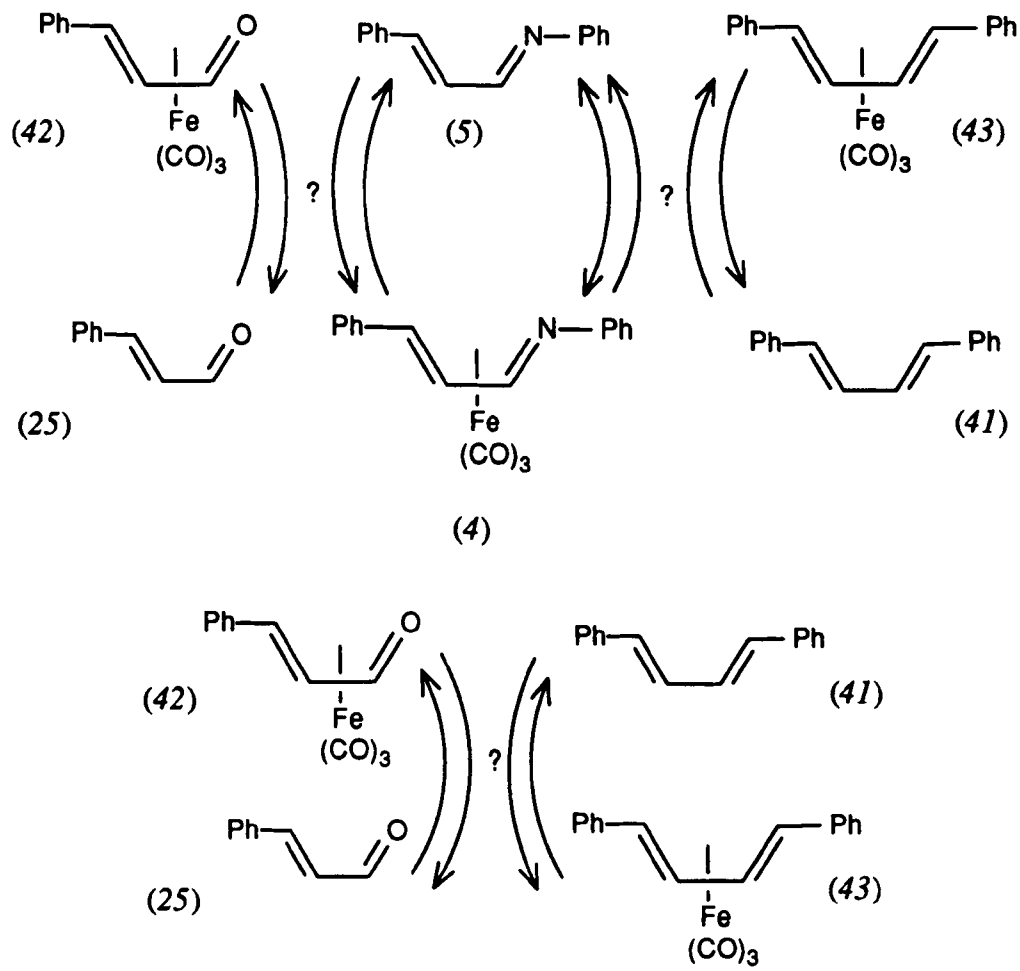
Transfer of the -Fe(CO)$_3$ unit in the reverse direction was then examined. (Cinnamaldehydeanil)tricarbonyliron(0) (*4*) and benzylideneacetone (*40*) were stirred in toluene at 84 °C for 90 hours. The dark brown reaction mixture was allowed to cool and then filtered through alumina. Concentration *in vacuo* and chromatography led to the recovery of starting complex (*4*) as brick red needles in 84% yield. The melting point, and i.r., ^{1}H n.m.r., and mass spectra of this product were identical to those obtained from the starting complex (*4*).



(*4*) (*40*)

6.3.2 Comparison of transfer reactions.

Having discovered that the -$Fe(CO)_3$ unit may be transferred from a 1-oxadiene complex to a 1-azadiene ligand, it was of interest to establish whether or not 1-azadiene complexes transfer -$Fe(CO)_3$ to diene ligands and whether or not diene complexes transfer -$Fe(CO)_3$ to 1-azadiene ligands. It was thus decided to examine the reactions outlined in Scheme 4, *i.e.* to study the transfer of the -$Fe(CO)_3$ unit between the closely related 1-oxadiene (*25*), 1-azadiene (*5*) and diene (*41*).

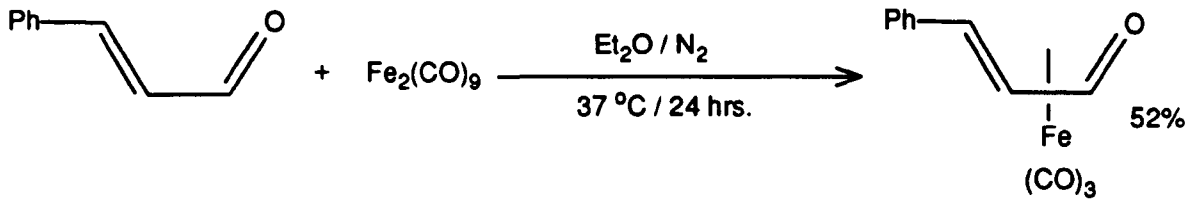


Scheme 4

6.3.2.1 Preparation of starting materials

(Cinnamaldehyde)tricarbonyliron(0) (*42*)[6] and (1,4-diphenylbutadiene)tricarbonyliron(0) (*43*)[33] were both synthesised by standard thermal complexation reactions.

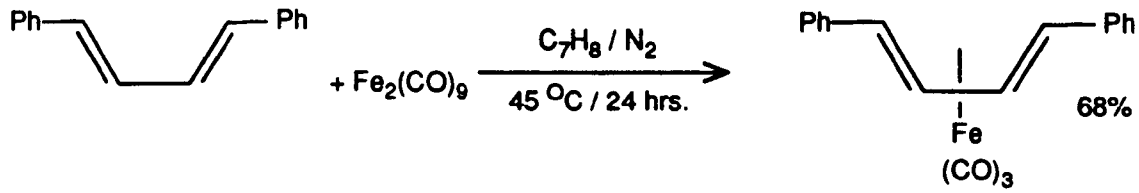
Cinnamaldehyde (*25*) and di-iron enneacarbonyl (*17*) were suspended in diethyl ether and stirred at reflux under a nitrogen atmosphere for 24 hours. The reaction mixture was filtered through alumina, concentrated *in vacuo* and then recrystallised from *n*-hexane to give (cinnamaldehyde)tricarbonyliron(0) (*42*) as brick red needles in 52% yield.



(*25*) (*17*) (*42*)

The ^{1}H n.m.r. spectrum of this material contained one-proton doublets at δ 3.29 (Ph-C<u>H</u>=) and δ 6.17 (Ph-CH=C<u>H</u>-), a five-proton doublet at δ 7.32 (Ph-), and a one-proton doublet at δ 7.65 (-C<u>H</u>=O). Complexation was confirmed by the presence of three strong C≡O absorptions in the i.r. spectrum at 2 075, 2 017 and 1 996 cm^{-1}. Both spectra were in good agreement with literature values[6]. The mass spectrum of this material contained peaks at 272 (M+1, 15%) and 133 (M-Fe(CO)$_3$), 100%).

1,4-Diphenylbutadiene (*41*) and di-iron enneacarbonyl (*17*) were suspended in toluene and stirred at 45 °C for 24 hours under a nitrogen atmosphere. The dark green reaction mixture was filtered and then concentrated *in vacuo* to leave a dark green solid. This solid was dissolved in a mixture of *n*-pentane and dichloromethane and filtered through alumina. The resulting solid was sublimed at reduced pressure to leave the complex (*43*) as golden yellow crystals in 68% yield. The complex (*43*) gave a ^{1}H n.m.r. spectrum containing two-proton doublets at δ 2.41 (2 x Ph-C<u>H</u>=) and δ 5.97 (2 x Ph-CH=C<u>H</u>-), and

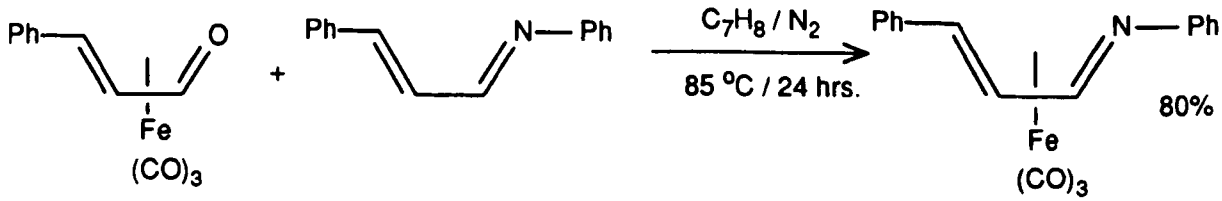


(*41*) (*17*) (*43*)

a ten-proton multiplet at δ 7.33 (2 x Ph-). Complexation was confirmed by the presence of strong C≡O stretches in the i.r. spectrum at 2 048 and 1 986 cm^{-1}. The mass spectrum contained a molecular ion (346, 22%) and peaks for the loss of one, two and three carbonyl groups (318, 67%; 290, 100%; and 262, 58% respectively). This analytical data and the melting point of the complex were in good agreement with literature values[33].

6.3.2.2 Transfer reactions

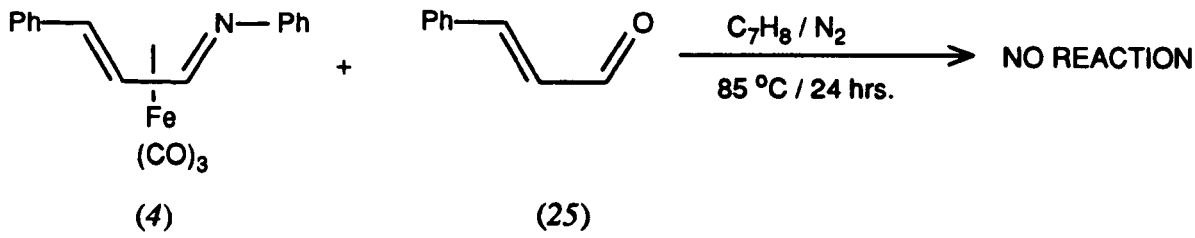
The reaction sequence outlined in Scheme 4 was then investigated. (Cinnamaldehyde)tricarbonyliron(0) (*42*) and cinnamaldehydeanil (*5*) were suspended in toluene and stirred at 85 °C for 24 hours under a nitrogen atmosphere. The reaction mixture was allowed to cool, filtered through alumina and concentrated *in vacuo*. Chromatography allowed the isolation of (cinnamaldehydeanil)tricarbonyliron(0) (*4*) as a red solid in 80% yield. The melting point, and i.r., ^1H n.m.r. and mass spectra of this solid were all in good agreement with those obtained on complex (*4*) formed by direct methods.



(*42*) (*5*) (*4*)

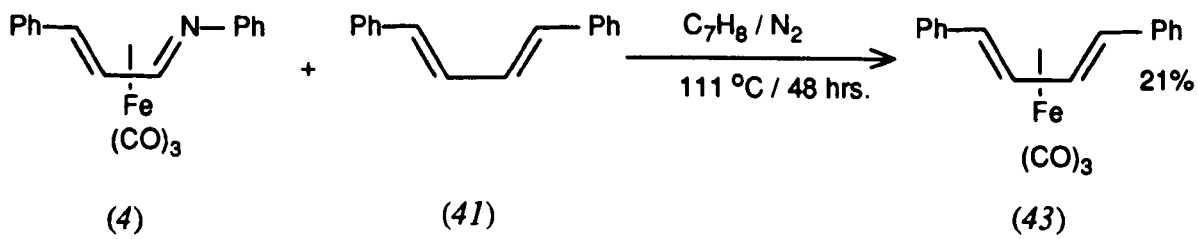
The 1-azadiene complex (*4*) and cinnamaldehyde (*25*) were then stirred in toluene at 85 °C for 24 hours under a nitrogen atmosphere. Standard work-up led to the isolation of starting complex (*4*) in 53% yield and there was no evidence that any oxadiene complex

(*42*) had been formed. Repetition of this reaction at a higher temperature (111 °C) for a longer time (48 hours) also led to the isolation of starting complex (*4*) (50% yield).



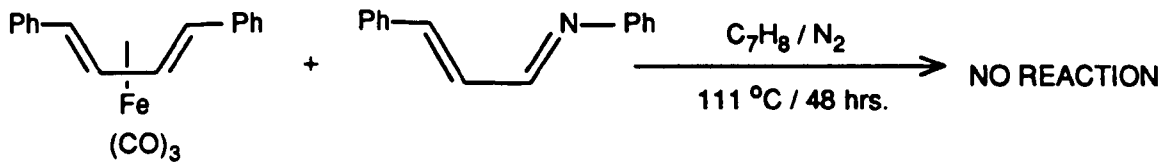
(*4*) (*25*)

There are no reports in the literature of 1-azadiene complexes being used as the source of -$Fe(CO)_3$ for a transfer reaction. (Cinnamaldehydeanil)tricarbonyliron(0) (*4*) was reacted with 1,4-diphenylbutadiene (*41*) in toluene and stirred at reflux under a nitrogen atmosphere for 48 hours. Standard work-up allowed the isolation of a yellow solid which was sublimed under reduced pressure to give (1,4-diphenylbutadiene)tricarbonyliron(0) (*43*) as yellow plates in 21% yield. The melting point, and i.r., ^1H n.m.r. and mass spectra were in excellent agreement with those obtained on complex (*43*) prepared by direct methods. This is the first use of a 1-azadiene complex as the source of -$Fe(CO)_3$ in a transfer reaction.



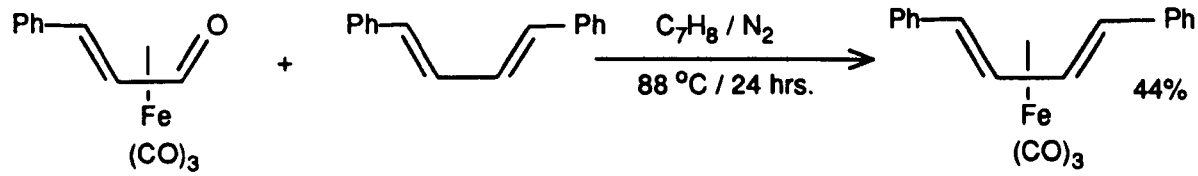
(*4*) (*41*) (*43*)

The reverse transfer was then examined. Diene complex (*43*) and cinnamaldehydeanil (*5*) were stirred in toluene at reflux for 48 hours under a nitrogen atmosphere. Standard work-up gave starting complex (*43*) in 57% yield.



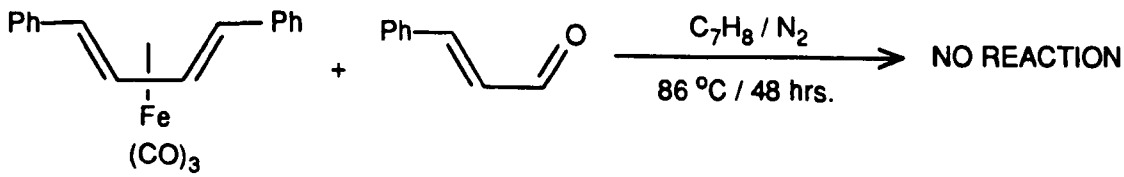
(*43*) (*5*)

To complete the investigation outlined in Scheme 4, the transfer of -$Fe(CO)_3$ between cinnamaldehyde (*25*) and 1,4-diphenylbutadiene (*41*) was examined. (Cinnamaldehyde)-tricarbonyliron(0) (*42*) and 1,4-diphenylbutadiene (*41*) were stirred in toluene at 88 °C for 24 hours under a nitrogen atmosphere. Work-up gave a yellow solid which was crystallised from *n*-hexane and sublimed at reduced pressure to leave (1,4-diphenylbutadiene)tricarbonyliron(0) (*43*) as yellow plates in 44% yield.



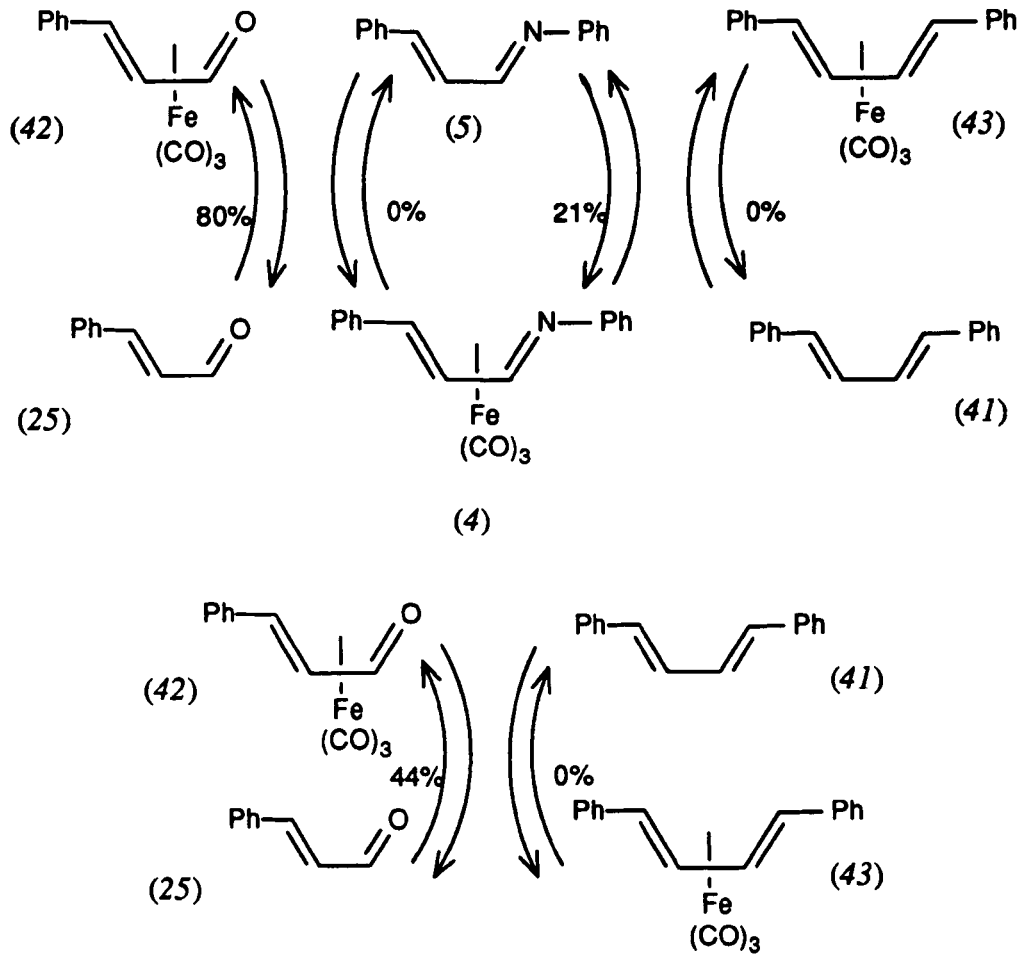
(*42*) (*41*) (*43*)

1,4-Diphenylbutadiene complex (*43*) and cinnamaldehyde (*25*) were stirred in toluene at 86 °C for 48 hours under a nitrogen atmosphere. Work-up led to the recovery of butadiene complex (*43*) in 92% yield.



(*43*) (*25*)

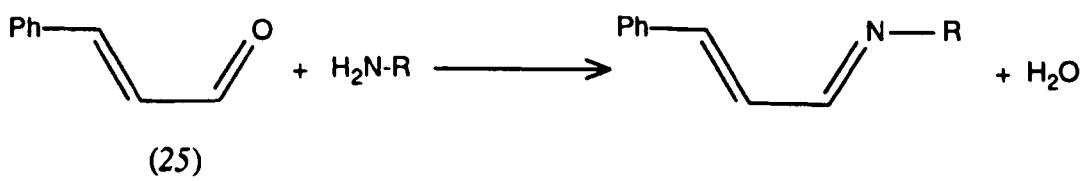
Scheme 4 can therefore be completed, overleaf:



Scheme 4

6.3.3 Further examples of O → N transfers.

Further examples of the transfer of the -$Fe(CO)_3$ unit from 1-oxadiene complexes to 1-azadiene ligands were then investigated. Several 1-azadiene ligands bearing different nitrogen-substituents were prepared *via* simple condensation reactions with cinnamaldehyde (*25*).



(*25*)

The 1-azadiene ligands were isolated and characterised. The results are summarised in Table 6.

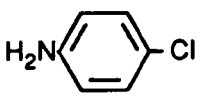
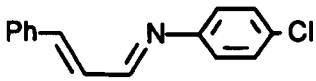
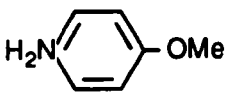
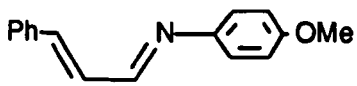
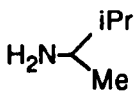
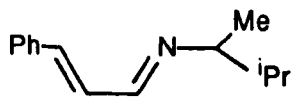
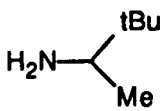
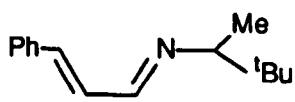
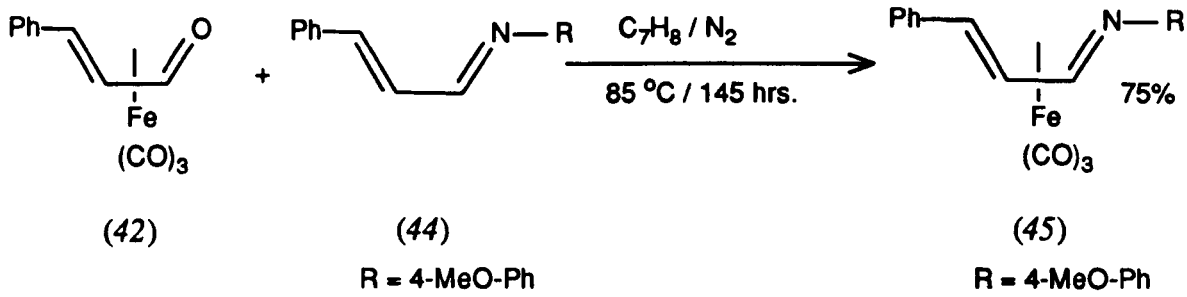
AMINE	AZADIENE	YIELD /%	LITERATURE REFERENCE
	 (*46*)	79	34, 35, 36
	 (*44*)	86	34, 35, 36
	 (*48*)	98	37
	 (*49*)	83	37

Table 6: Preparation of 1-azadiene ligands

Transfer reactions from (cinnamaldehyde)tricarbonyliron(0) (*42*) to these substituted 1-azadienes were then examined.

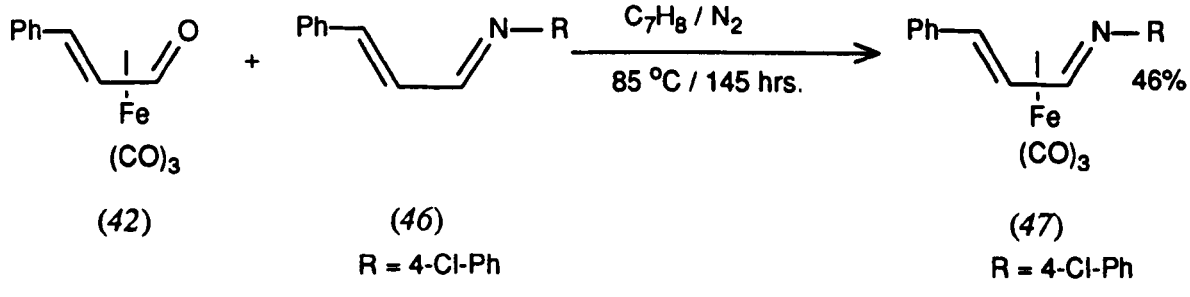
Reaction of *N*-4-methoxycinnamaldehydeanil (*44*) and (cinnamaldehyde)-tricarbonyliron(0) (*42*) in toluene at 85 °C for 14.5 hours gave (*N*-4-methoxycinnamaldehydeanil)tricarbonyliron(0) (*45*) in a 75% yield as a dark red solid, which was identified by comparison of its melting point, and i.r., and ^{1}H n.m.r.

spectra with literature values[6].



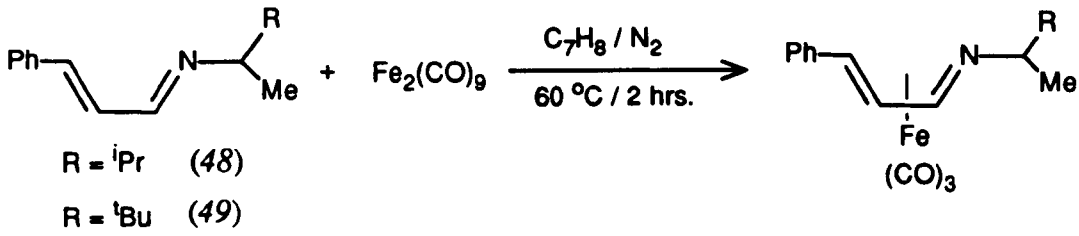
(*42*) (*44*) R = 4-MeO-Ph (*45*) R = 4-MeO-Ph

Similarly, the reaction of aldehyde complex (*42*) with *N*-4-chlorocinnamaldehydeanil (*46*) gave orange-red crystals which were identified as (*N*-4-chlorocinnamaldehydeanil)tricarbonyliron(0) (*47*) by comparison of its melting point, and i.r., and ^{1}H n.m.r. spectra with literature values[6].



(*42*) (*46*) R = 4-Cl-Ph (*47*) R = 4-Cl-Ph

The transfer of the $Fe(CO)_3$ unit from 1-oxadiene complex (*42*) to chiral 1-azadiene ligands was also investigated. The 'direct' complexations of chiral 1-azadienes (*48*) and (*49*) with di-iron enneacarbonyl (*17*) have been reported[37]:



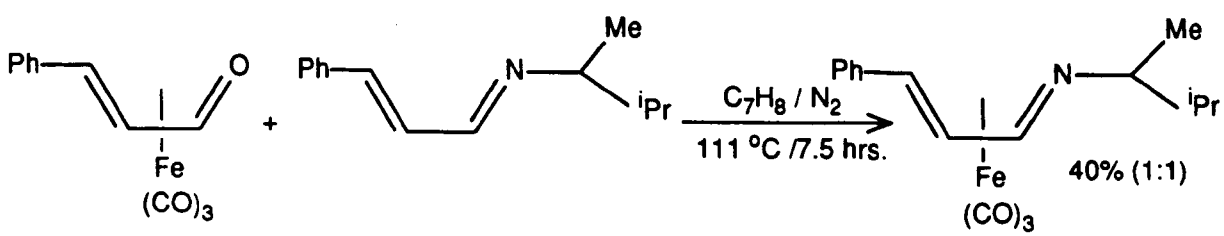
R = ^{i}Pr (*48*)

R = ^{t}Bu (*49*)

R		Yield %	Ratio of diastereoisomers
i_{Pr}	(*50*)	56	1:1
t_{Bu}	(*51*)	28	94:6

Complexation *via* -$Fe(CO)_3$ transfer from 1-oxadiene complex (*42*) was examined to determine whether or not this approach would lead to improved diastereoisomeric ratios.

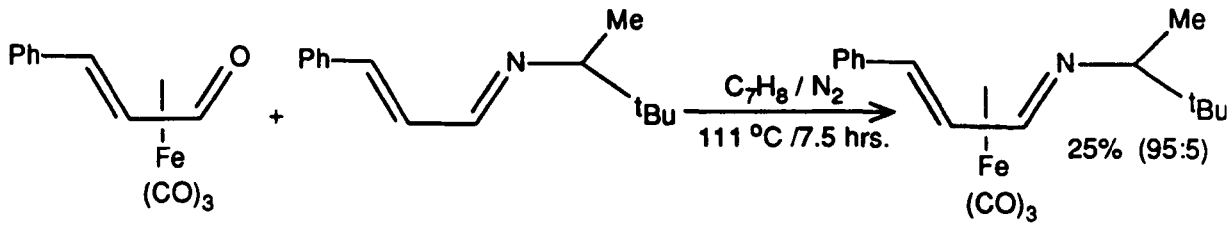
(Cinnamaldehyde)tricarbonyliron(0) (*42*) and *N*-α-*iso*-propylethylcinnamaldehydeanil (*48*) were stirred at reflux in toluene for 7.5 hours under a nitrogen atmosphere. Work-up gave an orange solid identified as a mixture of the two diastereoisomers of complex (*50*) in 46% yield. The two diastereoisomers were obtained in a 1:1 ratio based on the ratios of the integrals of peaks due to Ph-C<u>H</u>= protons (δ 2.95 and δ 3.00), and -N=C<u>H</u>- protons (δ 6.52 and δ 6.61) in the 400 MHz ^{1}H n.m.r. spectrum of the mixture. The ^{1}H n.m.r., i.r., and mass spectra obtained from the diastereoisomeric mixture of complexes were in good agreement with literature values[37].



(*42*) (*48*) (*50*)

Reaction of aldehyde complex (42) and *N*-α-*t*-butylethylcinnamaldehydeanil (*49*) led to

the isolation of azadiene complex (*51*) as yellow needles in 25% yield. The 400 MHz ^1H n.m.r. spectrum revealed this complex to be a mixture of diastereoisomers. Comparison of the integrals of the peaks due to Ph-C<u>H</u>= protons (δ 2.95 and δ 3.00) and -N=C<u>H</u>- protons (δ 6.50 and δ 6.81) revealed a diastereoisomeric ratio of 95:5 for complex (*51*). I.r., ^1H n.m.r., and mass spectral data were in good agreement with literature values[37].

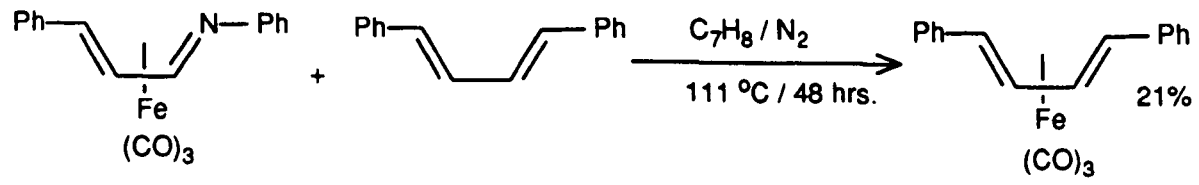


(*42*) (*49*) (*51*)

Thus, the complexation of chiral 1-azadiene ligands *via* transfer reactions from cinnamaldehyde complex (*42*) leads to the same degree of diastereo selectivity as the standard direct complexation procedure.

6.3.4 <u>The use of 1-azadiene complexes as a source of -Fe(CO)$_3$</u>.

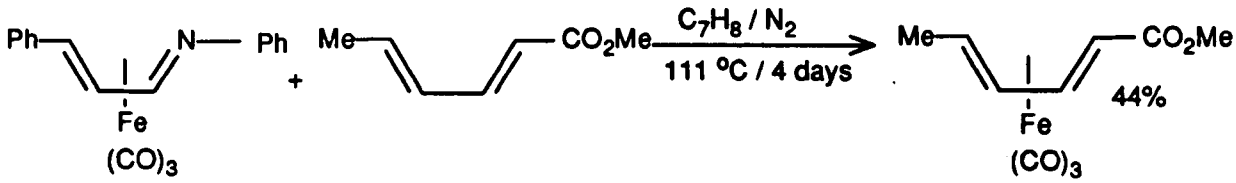
The transfer of -Fe(CO)$_3$ from (cinnamaldehydeanil)tricarbonyliron(0) (*4*) to 1,4-diphenylbutadiene (*41*) described above represented the first use of a 1-azadiene complex as the source of -Fe(CO)$_3$ in a transfer reaction.



(*4*) (*41*) (*43*)

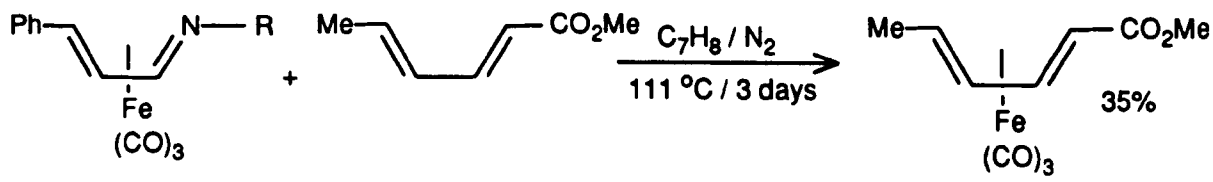
It was of interest, therefore, to see if 1-azadiene complex (*4*) could be used to transfer the Fe(CO)$_3$ unit to other diene ligands. Thus, (cinnamaldehydeanil)tricarbonyliron(0) (*4*) and methyl sorbate (*27*) were stirred in toluene at reflux for 4 days under a nitrogen

atmosphere. Work-up gave yellow crystals which were identified as (methyl sorbate)tricarbonyliron(0) (*28*) by comparison of their i.r., ^{1}H n.m.r. and mass spectra with literature values[26,38].



(*4*) (*27*) (*28*)

Use of a second 1-azadiene complex as a source of the $Fe(CO)_3$ unit was then examined. Methyl sorbate (*27*) and (*N*-4-chlorocinnamaldehydeanil)tricarbonyliron(0) (*47*) were stirred in toluene at reflux for 3 days under a nitrogen atmosphere. Filtration through alumina, concentration *in vacuo*, and chromatography allowed the isolation of methyl sorbate complex (*28*) in 35% yield. The ^{1}H n.m.r., i.r. and mass spectra were all in good agreement with literature values[26,38].

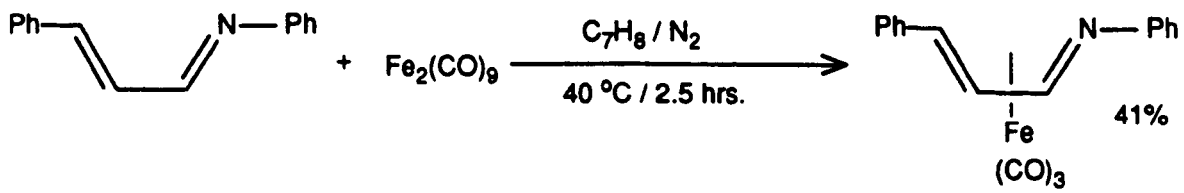


(*47*) (*27*) (*28*)

R = 4-Cl-Ph

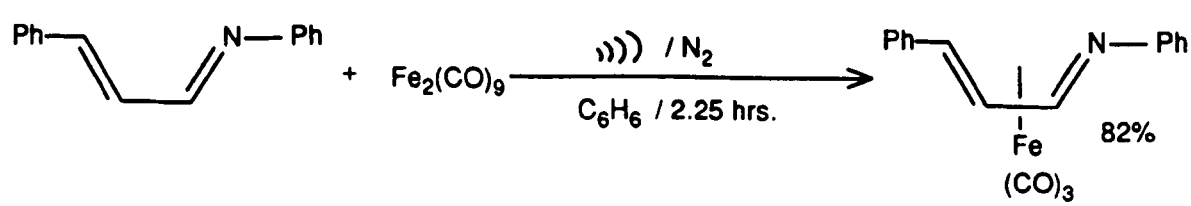
7. SUMMARY OF THE PREPARATION OF (1-AZADIENE) TRICARBONYLIRON(0) COMPLEXES

(Cinnamaldehydeanil)tricarbonyliron(0) (*4*) is traditionally prepared from cinnamaldehydeanil (*5*) in 41% yield by heating at 40 °C in toluene with 1 mole-equivalent of di-iron enneacarbonyl (*17*) under a nitrogen atmosphere[4].



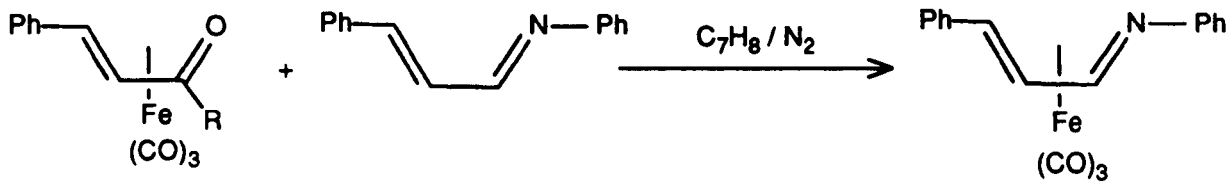
(*5*) (*17*) (*4*)

The yield of the standard thermal reaction is improved by the use of ultrasound; irradiation of anil (*5*) and 1 mole-equivalent of $Fe_2(CO)_9$ (*17*) in benzene for 2.25 hours produced complex (*4*) in 82% yield.



(*5*) (*17*) (*4*)

A novel approach to (1-azadiene)tricarbonyliron(0) complexes involves the use of a transfer reaction from oxadiene complexes. 1-Azadiene complexes were again obtained in improved yields compared to the standard thermal reaction.



(*29*) R = Me

(*42*) R = H

(*5*)

(*4*)

(R = Me, 62%)

(R = H, 80%)

DIELS-ALDER REACTIONS OF

(1-AZADIENE)TRICARBONYLIRON(0) COMPLEXES

8. INTERMOLECULAR CYCLOADDITION REACTIONS OF 1-AZADIENES

The Diels-Alder reaction is one of the most powerful methods for the preparation of carbocyclic six-membered rings. In one step two new carbon-carbon bonds are formed under good regiochemical and stereochemical control. In principle, the reaction of a diene or dienophile in which one carbon of a π-system is replaced by a nitrogen atom should provide a good method of preparing six-membered nitrogen-containing rings. This would be a useful reaction because:

(i) a wide range of nitrogen-containing compounds which potentially could replace the diene or dienophile component are available,

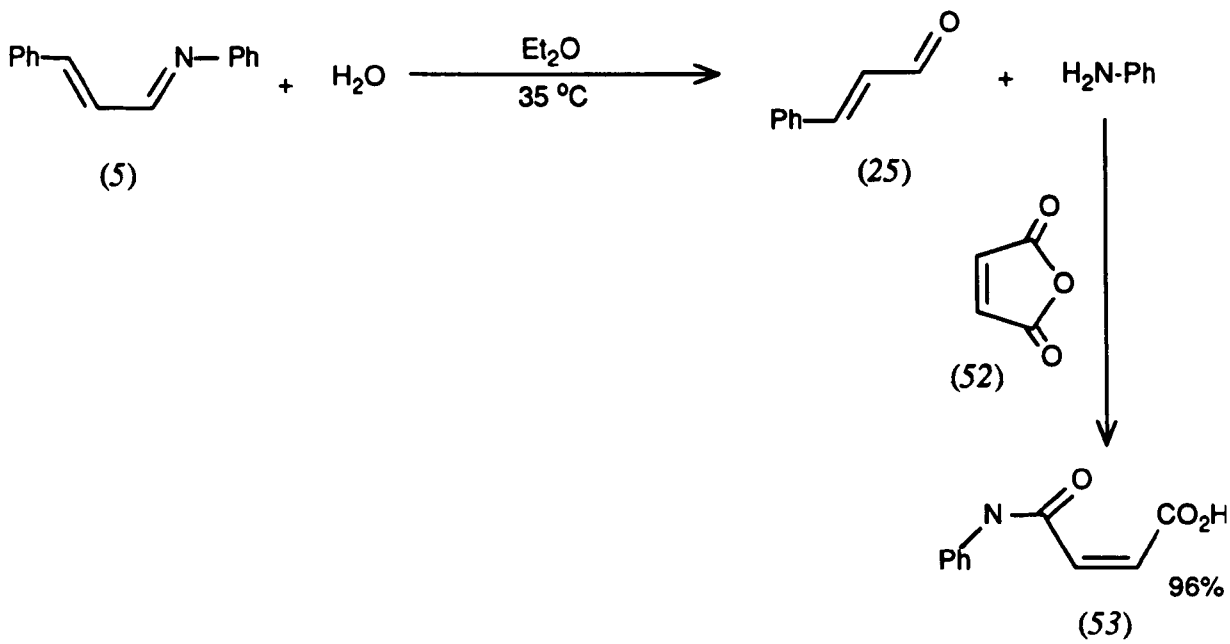
(ii) control could be exercised over the stereo- and regio-chemistry of the substituted heterocycles formed, and

(iii) the presence of an enamine functionality in some of the potential products should allow further structural elaboration if required.

There are many reported examples of the Diels-Alder reaction using imines as the dienophile[39], and using 2-azadienes as the diene component[40]. There are, however, only a few reports of Diels-Alder reactions using 1-azadienes as the diene component described below.

8.1 Problems With Cycloadditions.-

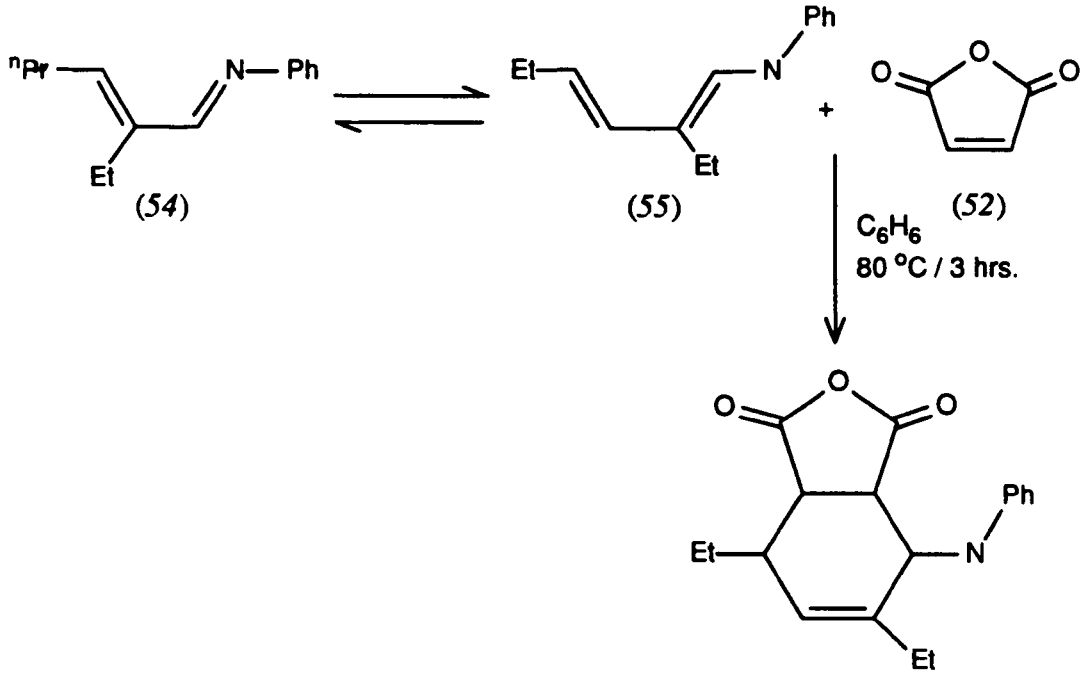
The first attempts to carry out Diels-Alder reactions on 1-azadienes were unsuccessful. The reaction of cinnamaldehydeanil (*5*) with maleic anhydride (*52*) resulted in the hydrolysis of the C=N bond in the anil (*5*), and the subsequent reaction of the aniline released with maleic anhydride (*52*) to give maleanilic acid (*53*)[41].



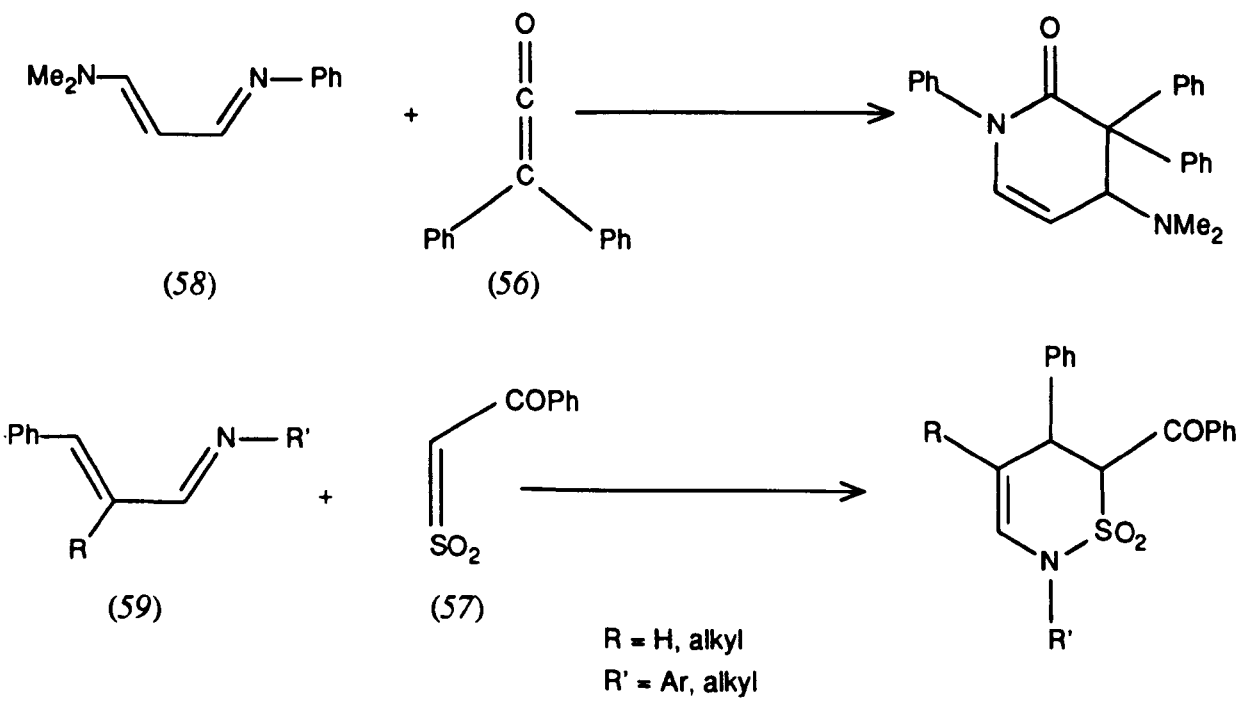
(5) (25) (52) (53)

Under strictly anhydrous conditions there was no reaction between cinnamaldehydeanil (*5*) and maleic anhydride (*52*).

1-Azadienes were found to take part in Diels-Alder reactions if they were capable of tautomerisation to a diene[42]. In these cases it is the diene component that actually undergoes the reaction. For example, the substituted 1-azadiene (*54*) rearranges to diene (*55*) which then gives a Diels-Alder reaction with maleic anhydride (*52*):



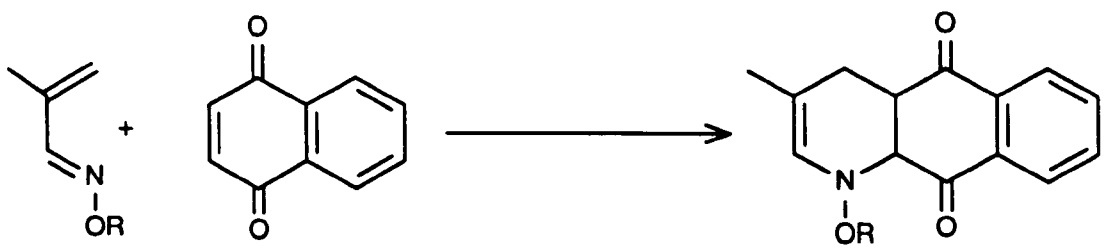
The reactive ketene (*56*) or benzoylsulfene (*57*) will act as dienophiles with 1-azadienes such as (*58*) and (*59*), and give heterocyclic compounds:



These reactions, however, although interesting, do not provide a generally useful method for carrying out Diels-Alder reactions on 1-azadienes. Attention turned, therefore, to methods of activating 1-azadienes to cycloaddition reactions.

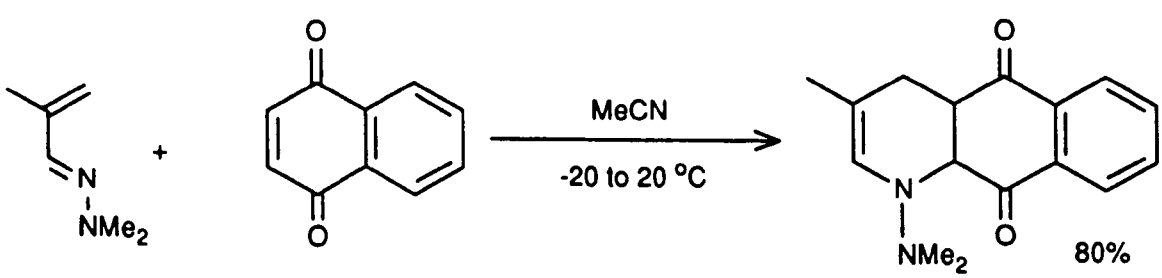
8.2 Activation at Nitrogen.-

The reason for the poor reactivity of the 1-azadienes towards electron-deficient dienophiles is thought to be the increased electrophilic character of the azadiene compared to the normal hydrocarbon diene system[43]. Incorporation of an electron-donating group into the azadiene system should increase the nucleophilic character of the azadiene and allow reactions with electron-deficient dienophiles to take place. Cycloaddition, and, ideally, the elimination of the activating group should then provide access to the desired six-membered heterocycles. This approach was demonstrated using the reactive dienophile naphthoquinone (*60*)[44]. The oxime ether (*61*) and anion (*62*) were reluctant to react with naphthoquinone (*60*).



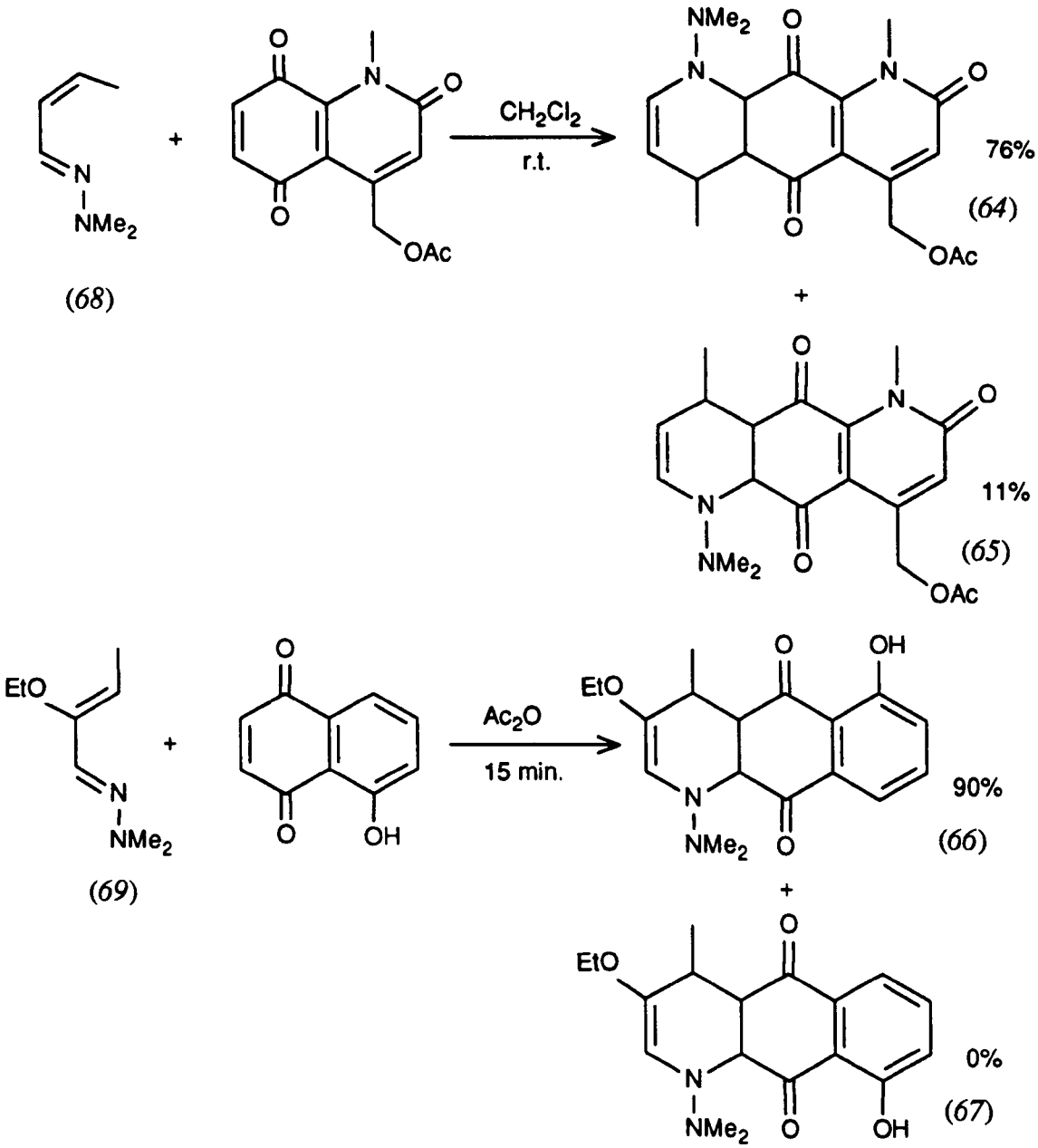
(*61*)	R = Me	(*60*)	MeCN /100 °C	0%
(*62*)	R = Li		Et_2O / -10 to 20°C	9%

Use of the strongly electron-donating dimethyl amino group (-NMe_2), however, resulted in the isolation of the unstable Diels-Alder adduct (*63*).



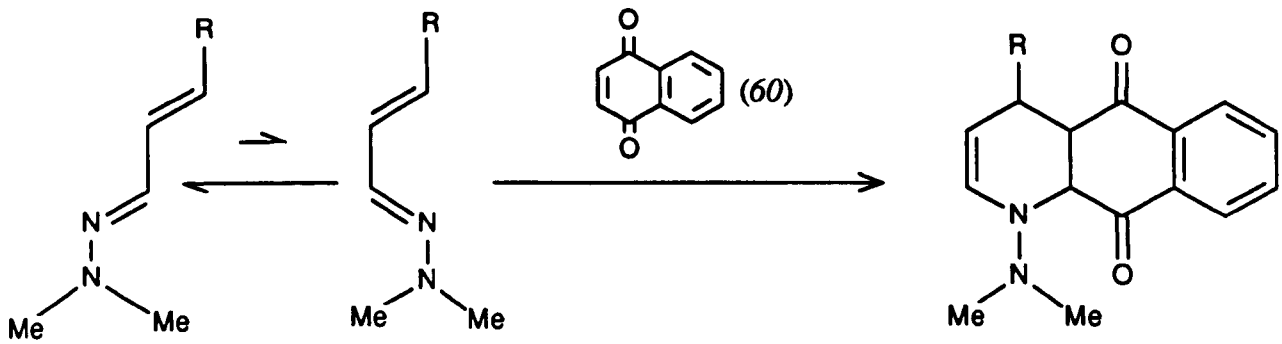
(*60*) (*63*)

The use of the dimethyl amino activating group is a successful development and it does allow Diels-Alder cycloadditions to be carried out on many simple 1-azadienes. For instance, it has been used in the regioselective synthesis of aza-anthraquinone derivatives (*64*)-(*67*) from the activated 1-azadienes (*68*) and (*69*)[45]:



One disadvantage with the use of the dimethyl amino group however, is that it places structural constraints on the 1-azadiene. In order for the dimethyl amino group to activate the 1-azadiene, the lone pair on the amine nitrogen must be of the correct geometry to interact with the diene system. Inspection of the u.v. spectra of 1-azadienes (*70*) and (*71*)

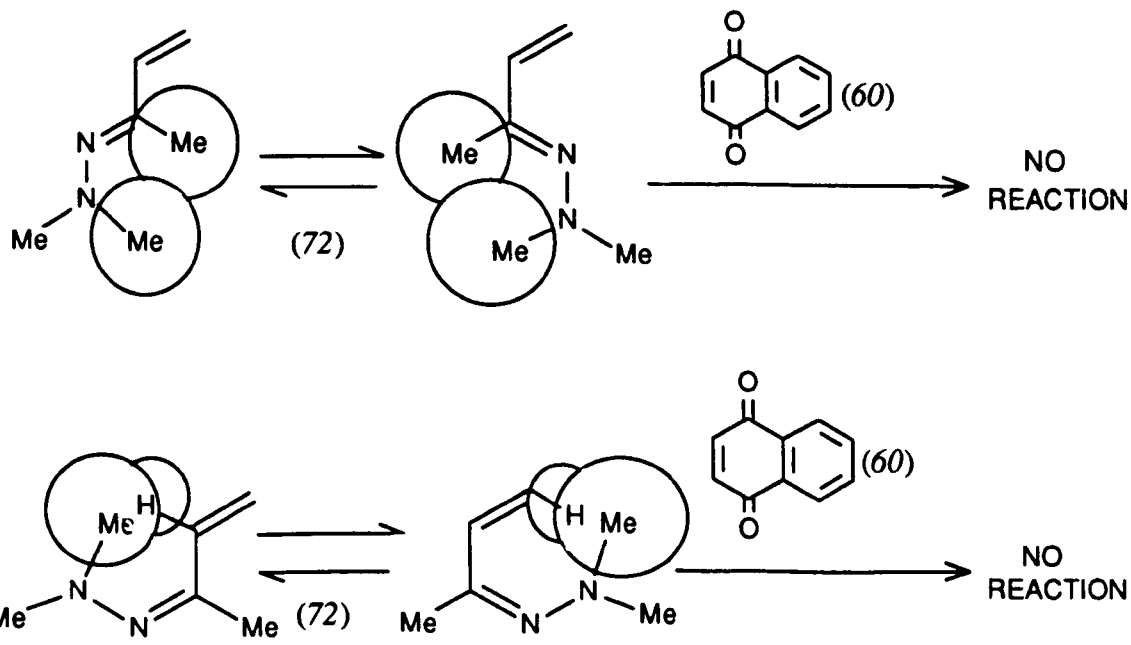
shows an absorption band at 276 nm, indicative of an interaction between the amine nitrogen lone pair and the diene system[44]. Both of these 1-azadienes undergo Diels-Alder cycloadditions with naphthoquinone (*60*) in good yield:



(*70*) R = H
(*71*) R = Me

R = H, 80%
R = Me, 60%

The u.v. spectrum of 1-azadiene (*72*), however, does not have an absorption band at 276 nm but absorbs at 222 nm. Steric hindrance prevents interaction of the lone pair with the diene π-system and cycloaddition reactions do not take place.



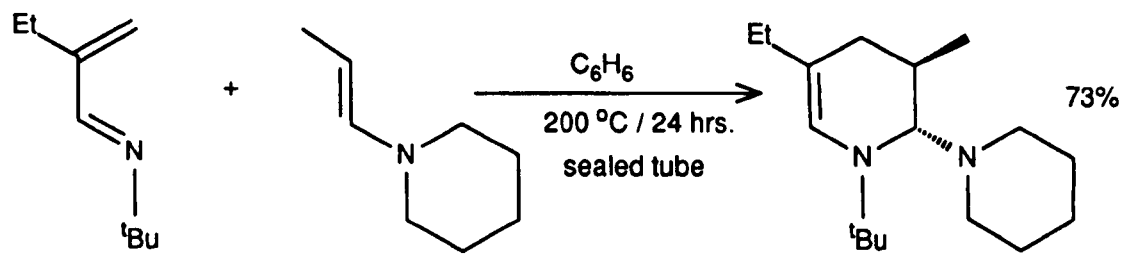
The dimethyl amino group, therefore, will only activate a 1-azadiene to Diels-Alder reactions provided that the 1-azadiene skeleton does not bear bulky substituents which

prevent interaction of the amine nitrogen lone pair with the 1-azadiene π-system.

Removal of the dimethyl amino group from the adducts after cycloaddition has taken place also presents a problem. This may be achieved by treatment of the adduct with three equivalents of zinc in acetic acid, followed by buffering to pH 8 using sodium carbonate solution[46]. Unfortunately this procedure also reduces the carbon-carbon double bond of the adduct, making further elaboration of the structure more difficult.

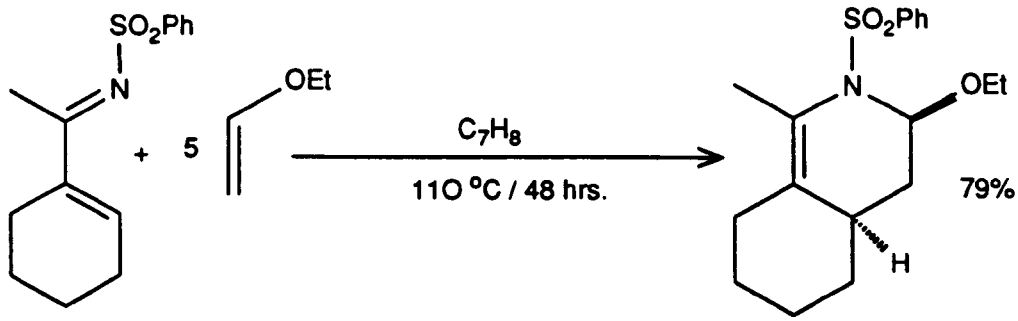
8.3 Use of Electron-rich Dienophiles.-

1-Azadienes are reluctant to participate in normal Diels-Alder reactions with electron-poor dienophiles because they have a strong electrophilic character due to the component nitrogen atom. This problem may be overcome by increasing the nucleophilic character of the azadiene with electron-donating substituents. An alternative approach lies in the use of electron-rich dienophiles. Electron-rich dienophiles such as enamine (*73*) will react with the electron-poor 1-azadienes to give cycloaddition products[47].

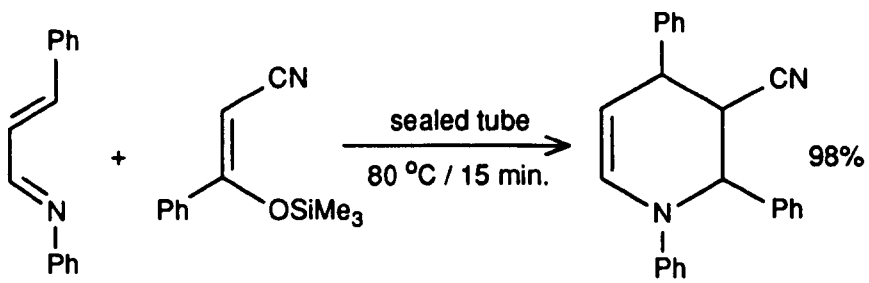


(*73*)

When electron-withdrawing substituents are added to the 1-azadiene reaction proceeds under slightly milder conditions[48].



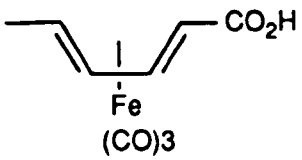
Unfortunately, this approach requires the use of harsh conditions, and often needs a large excess of dienophile in order to produce the desired cycloadducts. It is not, therefore, an ideal solution to the problem. Even with electron-rich dienophiles such as (*74*) a sealed tube reaction vessel was necessary for reaction to take place[49].



(*5*) (*74*)

9. CYCLOADDITIONS ON (CINNAMALDEHYDEANIL) TRICARBONYLIRON(0) (*4*)

As described above, efforts to induce Diels-Alder reactions between 1-azadienes and electron-poor dienophiles have included the substitution of electron-donating substituents onto the azadiene skeleton. This approach proved useful but was subject to restrictions in the structure of the 1-azadiene which could be activated in this way. The $Fe(CO)_3$ moiety in (diene)$Fe(CO)_3$ complexes behaves as a net inductive electron donor *e.g.* (sorbic acid)tricarbonyliron(0) (*75*) is a weaker acid than uncomplexed sorbic acid (*76*)[50]:



(*75*)

$pk_a = 7.25$

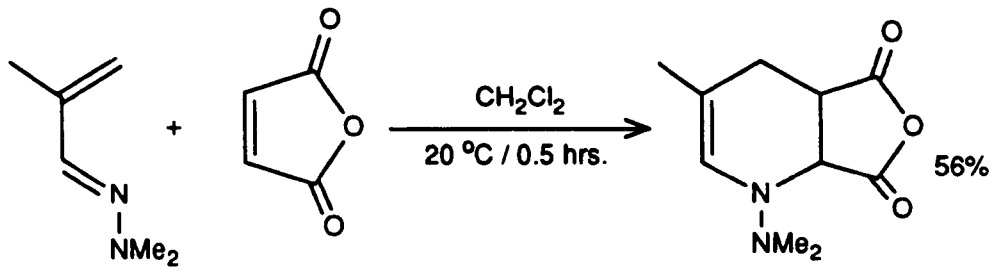
(*76*)

$pk_a = 7.00$

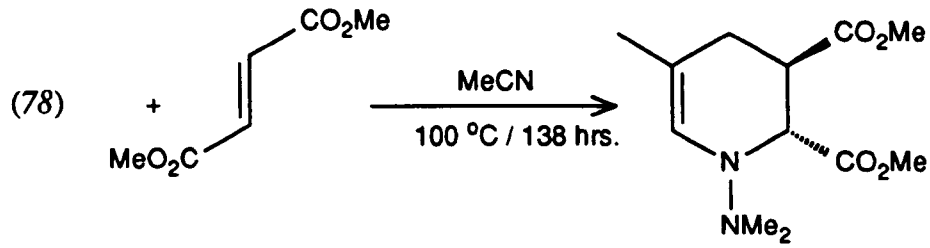
It was postulated, therefore, that the complexation of a 1-azadiene to an -$Fe(CO)_3$ group should activate the 1-azadiene to Diels-Alder reactions with electron-poor dienophiles.

9.1 1-Azadiene Complex Cycloaddition Reactions.-

1-Azadienes activated by a dimethyl amino group have been found to undergo Diels-Alder reactions with the reactive, electron-deficient dienophiles maleic anhydride (*52*) and dimethyl fumarate (*77*), which react with 1-azadiene (*78*) to give the expected cycloaddition products (*79*) and (*80*)[46]:



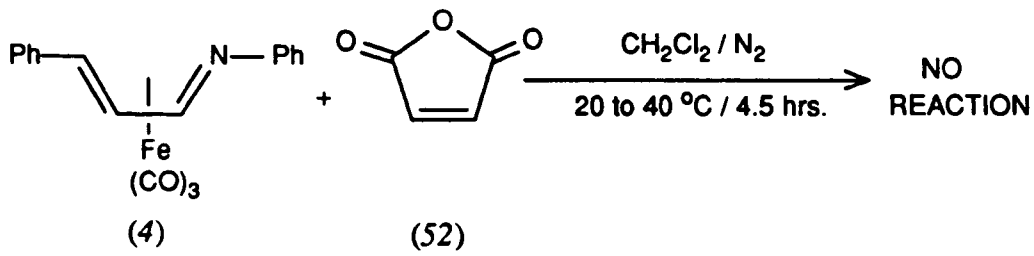
(*78*) (*52*) (*79*)



(*80*)

Reactions were investigated, therefore, between the dienophiles (*52*) and (*77*) and (cinnamaldehydeanil)tricarbonyliron(0) (*4*).

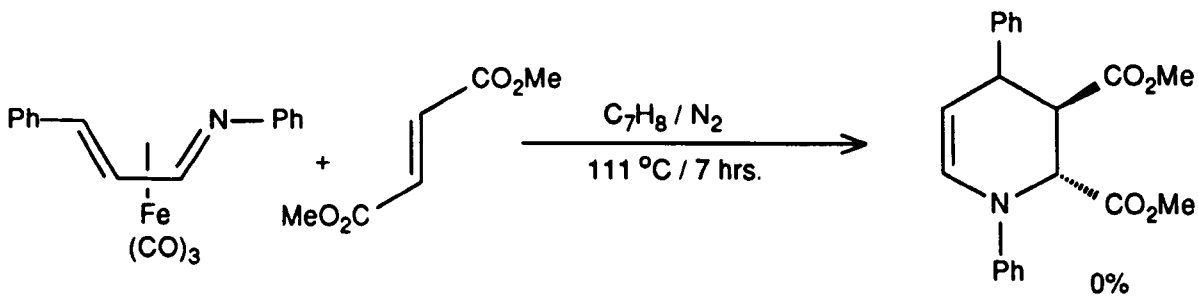
Anil complex (*4*) and 1 equivalent of maleic anhydride (*52*) were stirred together in dichloromethane at a range of temperatures between 20 and 40 °C for 4.5 hours. Examination of the crude reaction mixtures by t.l.c. and ^{1}H n.m.r. spectroscopy indicated that a cycloaddition reaction had not occurred. In each case there appeared to be only unreacted complex (*4*) and some uncomplexed anil (*5*). Filtration of the crude reaction mixtures through alumina, concentration *in vacuo* and recrystallisation from *n*-heptane allowed the recovery of starting complex (*4*) as orange-red needles in between 65 and 71% yield. The i.r., ^{1}H n.m.r., and mass spectra of this material were in good agreement with those obtained from the starting complex.



(*4*) (*52*)

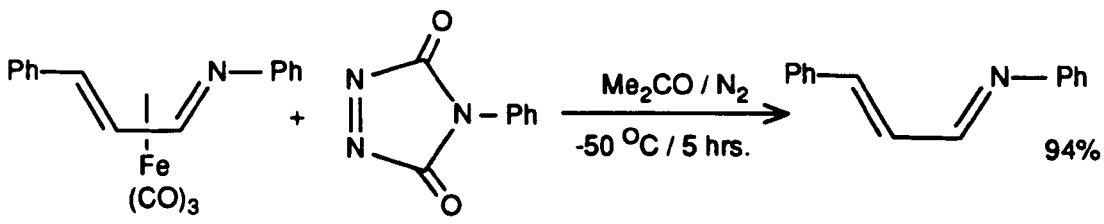
Repeating the reaction in methanol at 65 °C gave the same result, starting complex (*4*) being recovered in 77% yield on this occasion.

Dimethyl fumarate (*77*) was stirred with anil complex (*4*) in toluene at reflux under a nitrogen atmosphere for 7 hours. No trace of the cycloaddition product (*81*) could be detected by t.l.c. or ^{1}H n.m.r. spectroscopy. Work-up, as before, gave unreacted starting complex (*4*) in 75% yield.



(*4*) (*77*) (*81*)

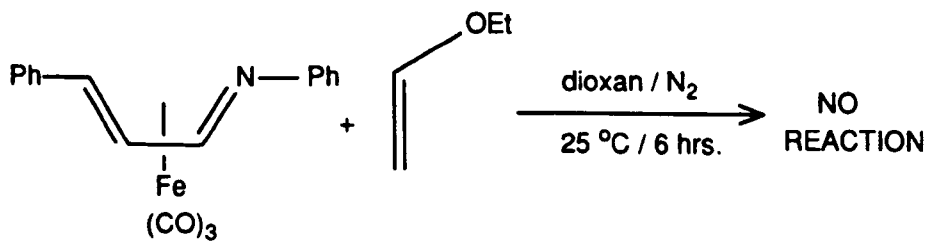
Phenyltriazolinedione (*82*), a more reactive electron-poor dienophile, was stirred with anil complex (*4*) in acetone at -50 °C under a nitrogen atmosphere for 5 hours. The reaction mixture was allowed to warm up to room temperature and then diluted with acetone. Filtration through alumina and then concentration *in vacuo* left uncomplexed cinnamaldehydeanil (*5*) in 94% yield.



(4) (82) (5)

As there was no indication of any cycloaddition reaction between cinnamaldehydeanil complex (*4*) and the electron-deficient dienophiles, the reaction between cinnamaldehydeanil complex (*4*) and an electron-rich dienophile was investigated.

(Cinnamaldehydeanil)tricarbonyliron(0) (*4*) and ethyl vinyl ether were stirred in dioxan at 25 °C for 6 hours under a nitrogen atmosphere. Concentration *in vacuo* and then chromatography allowed the isolation of a red solid. The i.r., ^{1}H n.m.r., and mass spectra of this solid revealed it to be unreacted starting complex (*4*), which had been recovered in 73% yield.



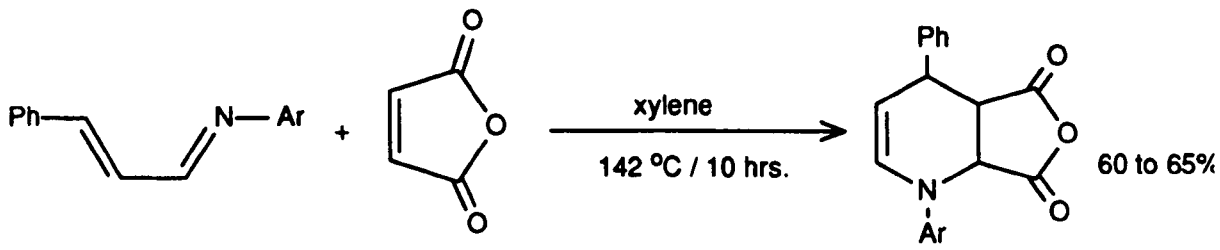
(4)

The behaviour of dienophiles with uncomplexed cinnamaldehydeanil (*5*) was then examined.

9.2 Cycloadditions on Cinnamaldehydeanil.-

Despite the problems experienced by most workers in achieving Diels-Alder cycloadditions of simple 1-azadienes, two reports of these reactions have appeared in the

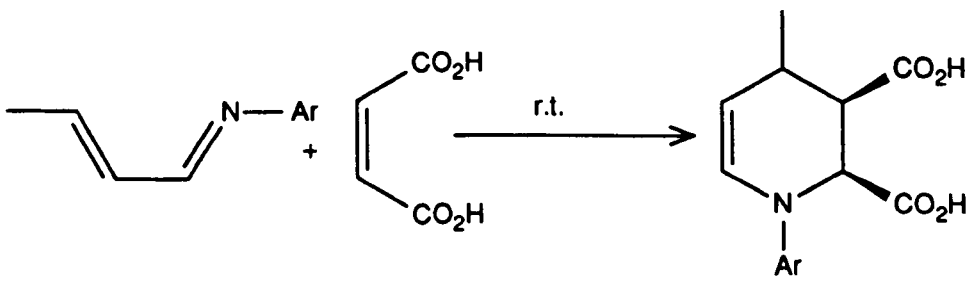
literature. Reaction of a range of *N*-aryl 1-azadienes (*83*) with maleic anhydride (*52*) in refluxing xylene is claimed to give a good yield of the appropriate cycloadducts (*84*)[51]:



(*83*) (*52*) (*84*)

Ar = Ph- / 2-Me-Ph- / 4-Me-Ph- / 4-MeO-Ph- / 4-Cl-Ph- / naphthyl-

Stirring simple 1-azadienes with maleic acid (*85*) at room temperature was also purported to give cycloadducts[52]:



(*85*)

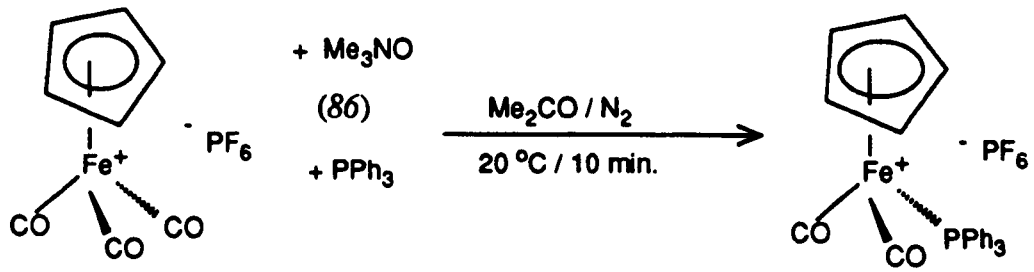
Ar = H- / Me- / Ph- /furyl- /thienyl-

The reaction of uncomplexed cinnamaldehydeanil (*5*) and maleic anhydride (*52*) was thus investigated. Stirring the two compounds in dichloromethane at room temperature for 5 hours, in methanol at reflux for 7 hours, or in xylene at reflux for 10 hours gave a turbid, yellow solution. Filtration through alumina and concentration in vacuo left cinnamaldehyde (*25*) in each case as a golden yellow liquid in between 68 and 79% yield. The ^{1}H n.m.r. and i.r. spectra of this liquid were in good agreement with literature values[53]. It appears, therefore, that reaction of anil (*5*) with the dienophile used led only to hydrolysis of the C=N bond in the 1-azadiene.

In view of the results described above, complexation with -$Fe(CO)_3$ appears to protect the 1-azadiene from hydrolysis under the reaction conditions. The -$Fe(CO)_3$ unit, however, does not activate the 1-azadiene towards Diels-Alder type reactivity with electron-rich or electron-deficient dienophiles.

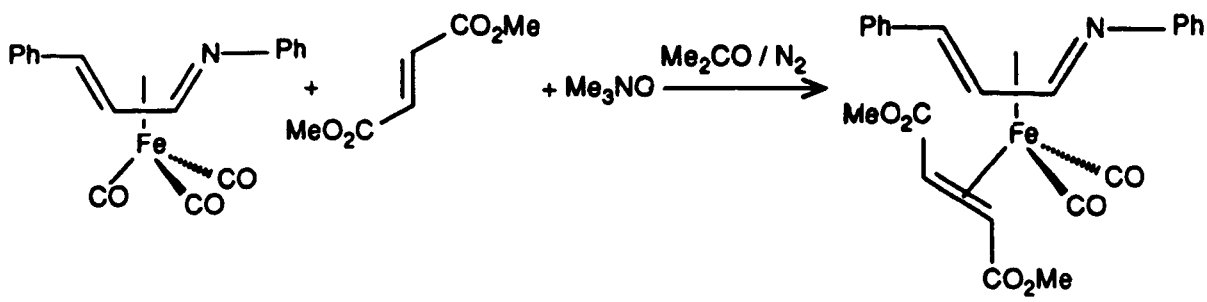
9.3 Metal-Mediated Reactions.-

Treatment of organotransition metal carbonyl complexes with trimethyloxamine (*86*) is known to result in the stepwise removal of carbon monoxide ligands and their replacement by other available donor ligands[54]. For example, cationic iron complex (*87*) has one of its carbon monoxide ligands removed by trimethyloxamine (*86*), leaving a free coordination site to accept a triphenylphosphine ligand:



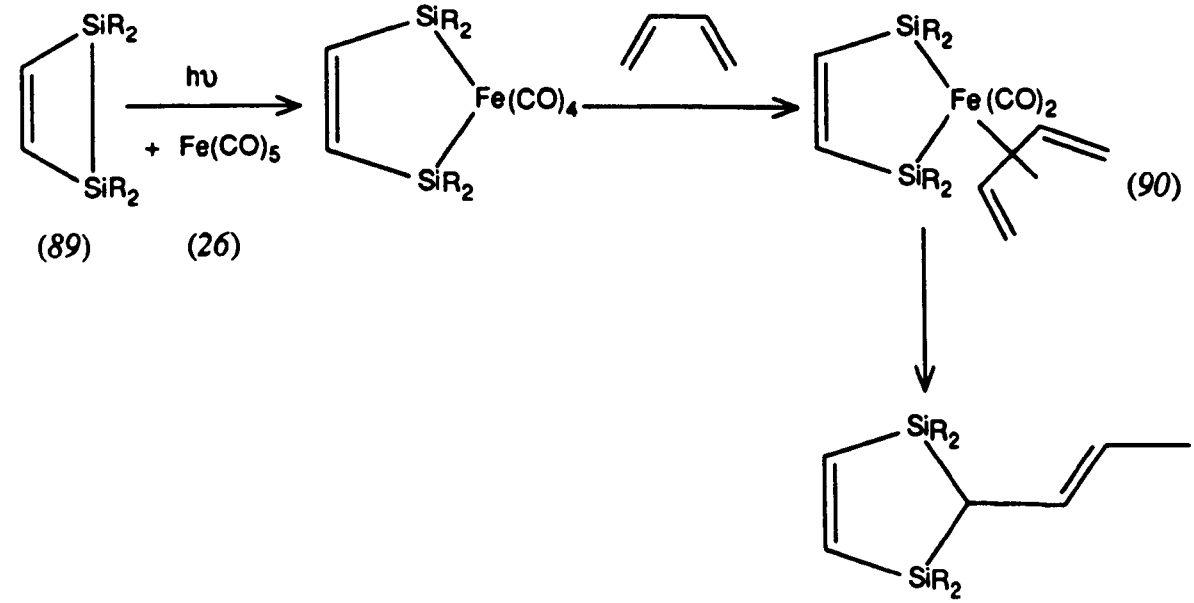
(*87*)

It was postulated that treatment of (cinnamaldehydeanil)tricarbonyliron(0) (*4*) with trimethyloxamine (*86*), in the presence of a dienophile would lead to the formation of complex (*88*):



(*4*) (*77*) (*86*) (*88*)

Thus, the iron atom would draw the 1-azadiene and dienophile together and thereby promote a reaction between them. It is of note that iron carbonyl complexes have been reported to catalyse the reaction of 1,2-disilacyclobutenes (*89*) with dienes *via* a similar intermediate (*90*)[55].



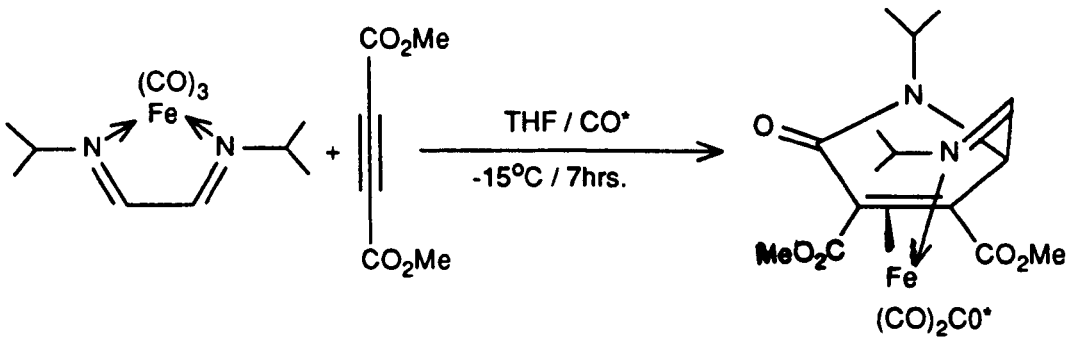
(*89*) (*26*)

(Cinnamaldehydeanil)tricarbonyliron(0) (*4*) and 2 mole-equivalents of dimethyl fumarate (*77*) were stirred in acetone with 4 mole-equivalents of trimethyloxamine (*86*) at room temperature under a nitrogen atmosphere. After 5 hours, the cloudy orange solution was filtered through alumina and concentrated *in vacuo* to leave the starting complex (*4*) and dimethyl fumarate (*77*). No trace of any other product could be found by ^{1}H n.m.r. spectroscopy or t.l.c. analysis. Recrystallisation of the crude product from *n*-heptane

allowed the isolation of complex (*4*) in 75% yield. The i.r., ^{1}H n.m.r., and mass spectra of this complex were in good agreement with those obtained from the starting material.

9.4 Dihydropyridine Formation.-

The reactions of (1,4-diazadiene)tricarbonyliron(0) complexes, such as complex (*91*) below, with dimethylacetylenedicarboxylate, DAD, have been reported[56]. Under a carbon monoxide atmosphere reaction takes place to form the σ,π-complex (*92*).

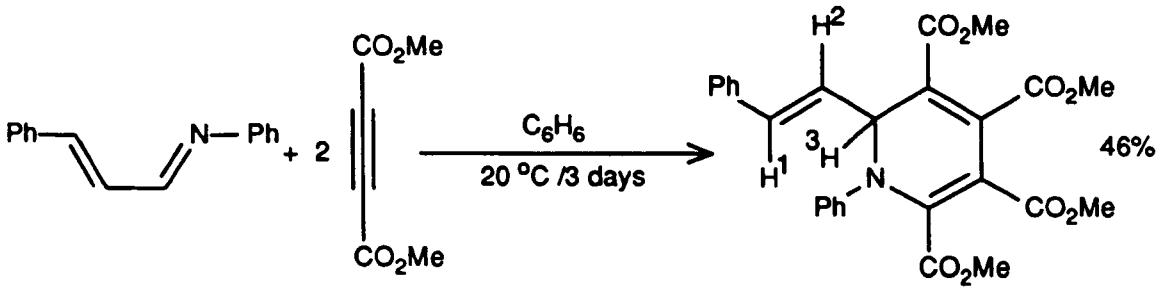


(*91*) (92)

It was decided, therefore, to investigate the reaction of (cinnamaldehydeanil)-tricarbonyliron(0) (*4*) with DAD under a carbon monoxide atmosphere.

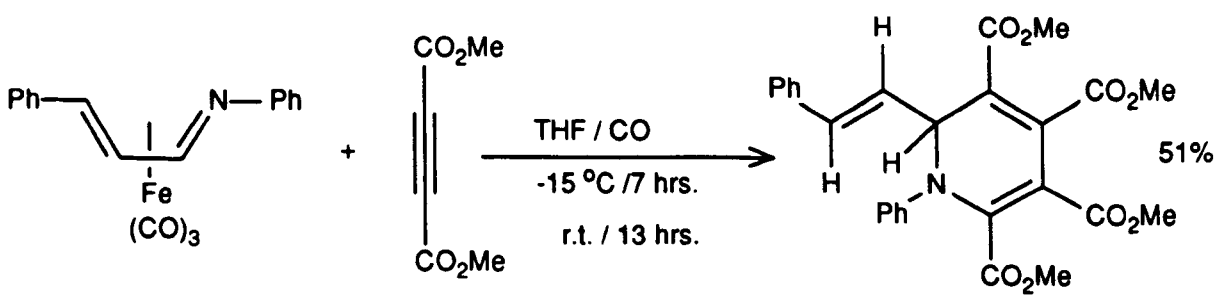
The tricarbonyliron(0) complex (*4*) was treated with an excess of DAD in THF at -15 °C and stirred for 7 hours under a carbon monoxide atmosphere. The reaction mixture was allowed to warm up to room temperature over 2 hours and then stirred for an additional 11 hours. Concentration *in vacuo* and chromatography gave material which, when recrystallised from methanol, produced pale yellow plates of melting point 158-161 °C. The ^{1}H n.m.r. spectrum contained four sharp three-proton singlets between δ 3.55 and δ 3.90. In addition, two one-proton doublets at δ 5.45 (*J* 5.5 Hz) and δ 6.70 (*J* 18 Hz), a one-proton double doublet at δ 6.30 (*J* 5.5 and 18 Hz), and a five-proton multiplet at δ 7.35 were also present. The i.r. spectrum was dominated by organic carbonyl stretches between 1 750 and 1 700 cm^{-1}. A literature search revealed the following reaction, in which anil (*5*) reacts with DAD to undergo an addition to the carbon-nitrogen double bond

resulting in dihydropyridine (*93*)[57].



(*5*) (*93*)

Substituted dihydropyridine (*93*) had a melting point of 161-165 °C. The ^{1}H n.m.r. spectrum contained four sharp singlets between δ 3.60 and δ 3.95 (-$CO_2C\underline{H}_3$), doublets at δ 5.45 (H^1) and δ 6.70 (H^3), a double doublet at δ 6.30 (H^2) and a multiplet at δ 7.35 (Ph-). The i.r. spectrum was in good agreement with that for the unidentified yellow plates. The literature data[57] suggested that the product of the reaction between cinnamaldehydeanil complex (*4*) and DAD is the substituted dihydropyridine (*93*). This was in good agreement with the mass spectrum (where the expected molecular ion was present and the base peak corresponded to the loss of one -CO_2CH_3 group).



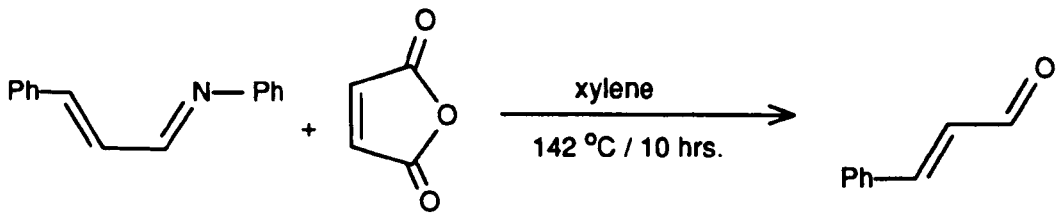
(*4*) (*93*)

Performing the reaction between complex (*4*) and DAD under a nitrogen, rather than a carbon monoxide atmosphere resulted in the recovery of unreacted complex (*4*) (74%), and DAD (60%). No trace of any dihydropyridine species was found by ^{1}H n.m.r. spectroscopy.

The results suggest that carbon monoxide from the reaction atmosphere displaces the carbon-nitrogen double bond from the iron atom to form a tetracarbonyliron species. DAD could then react with the exposed carbon-nitrogen double bond. Further incorporation of carbon monoxide presumably then leads to iron pentacarbonyl (*26*) and the liberated dihydropyridine (*93*).

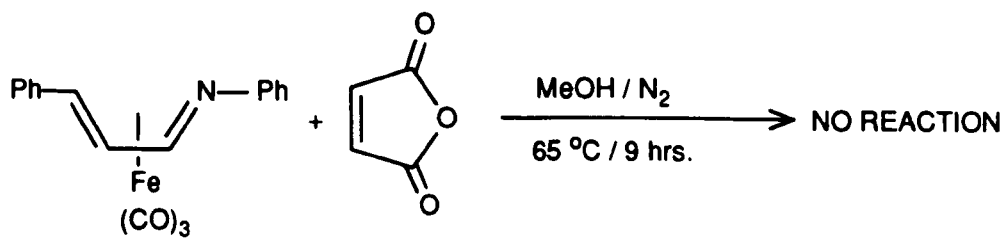
10. SUMMARY OF CYCLOADDITIONS ON (1-AZADIENE)TRICARBONYLIRON(0) COMPLEXES

Cinnamaldehydeanil (*5*), a typical 1-azadiene compound, was found to be unreactive with respect to Diels-Alder reactions. Treatment of the anil (*5*) with maleic anhydride (*52*) resulted in the hydrolysis of the carbon-nitrogen double bond.



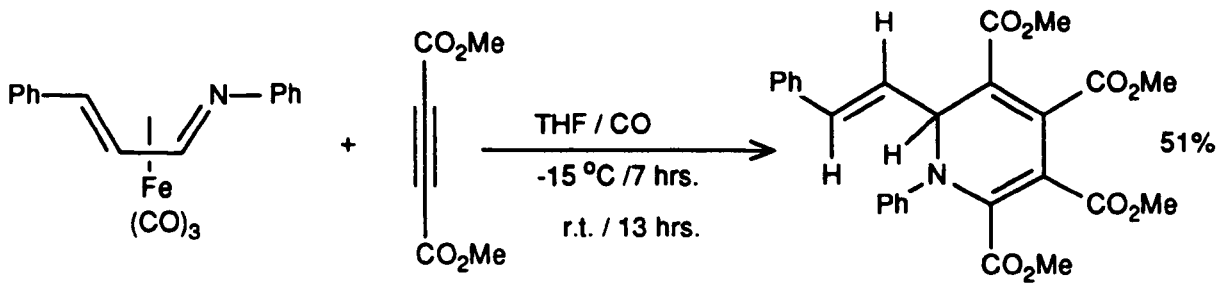
(*5*) (*52*) (*25*)

Introduction of a tricarbonyliron(0) moiety did not activate the complex towards Diels-Alder reactions but did prevent hydrolysis of the carbon-nitrogen double bond.



(*4*) (*52*)

Additions to the carbon-nitrogen double bond of the anil complex (*4*) could be accomplished with an excess of dimethyl acetylenedicarboxylate (DAD) to form 1-phenyl-2-styryl-1,2-dihydropyridintetracarboxylic acid-(3,4,5,6)-tetramethyl ester (*93*). A carbon monoxide atmosphere was found to be essential for this reaction to proceed.

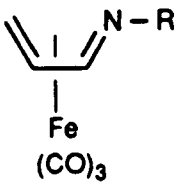


(*4*) (*93*)

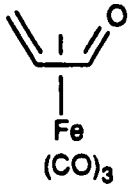
(2-AZADIENE)TRICARBONYLIRON(0) COMPLEXES

11. (HETERADIENE)TRICARBONYLIRON(0) COMPLEXES

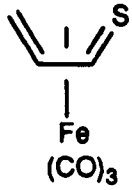
A range of (heteradiene)tricarbonyliron(0) complexes *(2)*, *(94)*, *(95)*, and *(3)* have been prepared and the bonding between the organic ligand and the tricarbonyliron moiety studied.



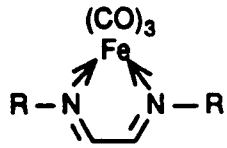
(2)



(94)

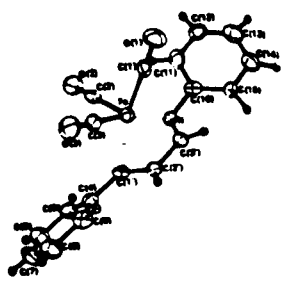


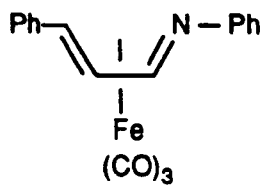
(95)



(3)

(1-Azadiene)tricarbonyliron(0) complexes (2) have been discussed in detail in Chapter Five. The bonding has been studied by a wide range of techniques and the structure of (cinnamaldehydeanil)tricarbonyliron(0) *(4)*, a representative 1-azadiene complex, was finally confirmed by X-ray crystallographic studies[9]:



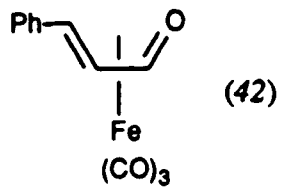


(4)

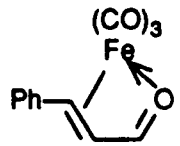
The ligand was found to be coordinated *via* bonding between the metal and the carbon-carbon and carbon-nitrogen π-bonds. The lone pair on the nitrogen atom was found not to play an important role in the bonding.

(1-Oxadiene)tricarbonyliron(0) complexes *(94)* have also been investigated. As with 1-azadiene complexes[2], 1-oxadiene complexes *(94)* may, in principle, adopt two different bonding modes. The 1-oxadiene ligand could be coordinated to the metal atom *via* bonds between the metal atom and the carbon-carbon and carbon-oxygen π-bonds (Diagram 2),

similar to 'Bonding Mode A' for 1-azadiene compounds. Alternatively, the ligand could be coordinated *via* a bond to the carbon-carbon π-bond, plus a σ-bond between the metal and a lone pair on the oxygen atom (*c.f.* 'Bonding Mode B' for 1-azadiene complexes).



(*42*)



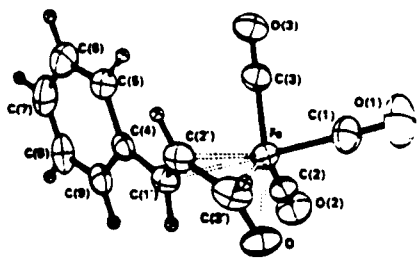
(*42*)

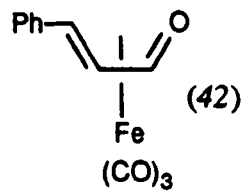
π,π-bonding

σ,π-bonding

Diagram 2: Bonding modes for 1-oxadiene complexes

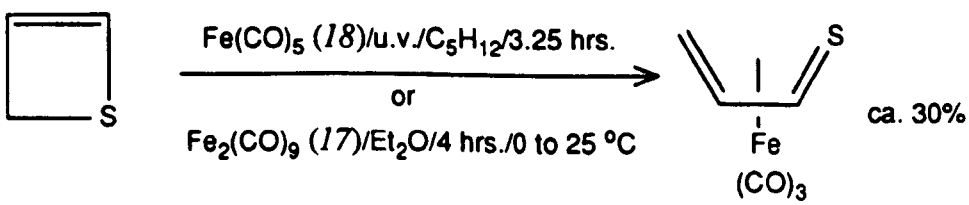
X-ray crystallographic studies on (cinnamaldehyde)tricarbonyliron(0) (*42*), revealed that the bonding is *via* two π-bonds, *i.e.* 'Bonding Mode A'[58]. No involvement of the two oxygen lone pairs in bonding could be detected.





(*42*)

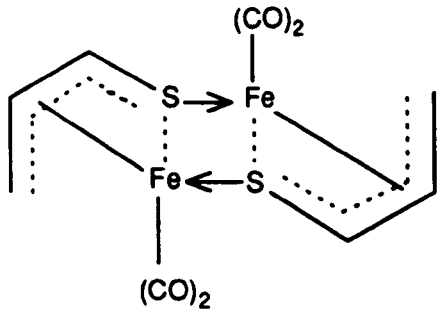
Treatment of thiacyclobutenes (*96*) with $Fe(CO)_5$ (*18*) in pentane, or $Fe_2(CO)_9$ (*17*) in diethyl ether, allows the isolation of (1-thiadiene)tricarbonyliron(0) complexes (*95*)[59].



(*96*)

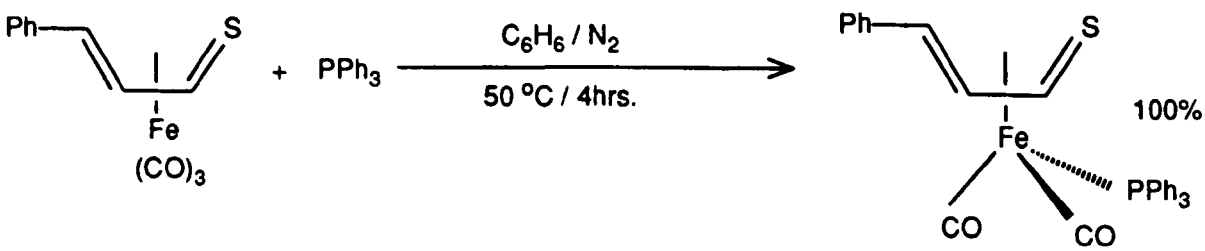
(*95*)

However, thiadiene complexes such as (*95*) are thermally unstable and readily lose carbon monoxide to give dimers *e.g.* (*97*)[59].



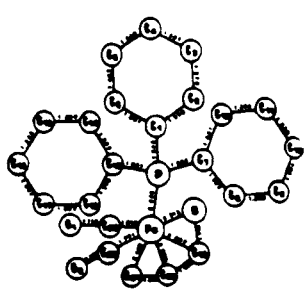
(*97*)

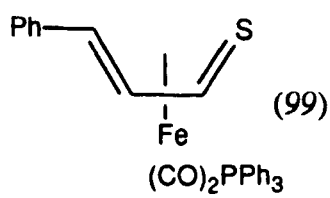
If triphenylphosphine is substituted for one carbon monoxide ligand, a stable, crystalline, monomeric (1-thiadiene)triphenylphosphinedicarbonyliron(0) complex is produced *e.g.* the phenyl substituted (1-thiadiene)tricarbonyl complex (*98*) readily forms a dimer, but substitution with triphenylphosphine allows the isolation of complex (*99*) as a crystalline solid. X-ray crystallographic studies on this solid clarified the structure of 1-thiadiene complexes[60].



(*98*) (*99*)

1-Thiadiene complexes were found to be bonded to the iron atom through their carbon-carbon and carbon-sulphur π-bonds. There was no evidence of any involvement of the sulphur lone pairs in the bonding.

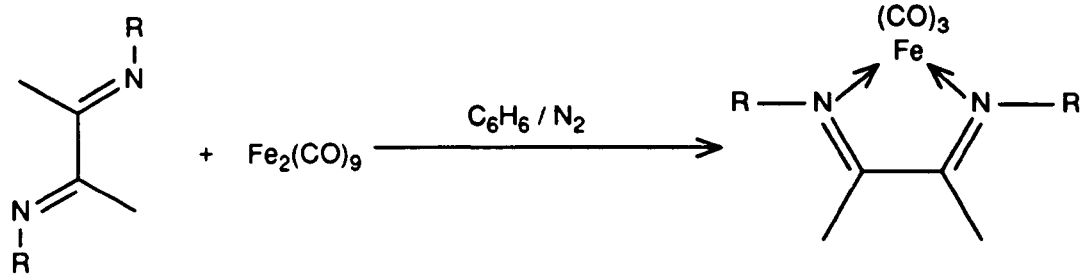




(*99*)

The synthesis of tricarbonyliron(0) complexes of nitrogen-containing diene systems has not been limited to (1-azadiene)tricarbonyliron(0) complexes. A series of (1,4-diazadiene)tricarbonyliron(0) complexes (*3*), where two carbon atoms from the butadiene system have been replaced by nitrogen atoms, has also been prepared.

Treatment of diacetylanil (*100*) with $Fe_2(CO)_9$ (*17*) in benzene at 40 °C for 3.5 hours, or of diacetyl-*n*-butylimine (*101*) with $Fe_2(CO)_9$ (*17*) in benzene at 40 °C for 7 hours, allows the preparation of (1,4-diazadiene)tricarbonyliron(0) complexes (*102*) and (*103*)[4].

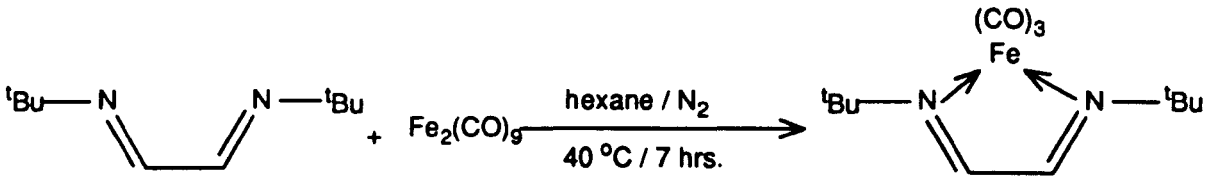


(*100*) R = Ph (*17*) 40 °C / 3.5 hrs. (*102*) R = Ph, 39%

(*101*) R = ^{n}Bu 40 °C / 7 hrs. (*103*) R = ^{n}Bu, 12%

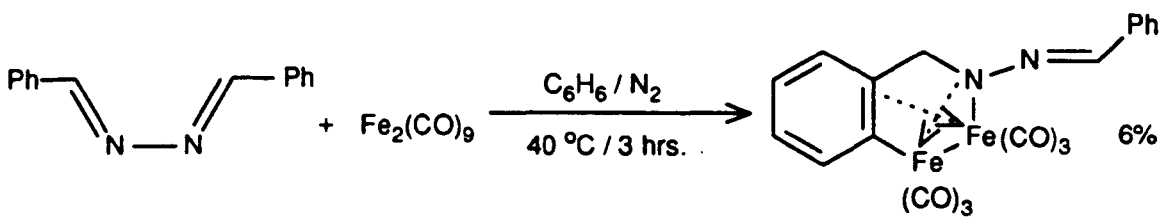
The ^{1}H n.m.r. spectrum for 1,4-diazadiene complex (*103*) suggested bonding was *via* the nitrogen lone pairs. In (1-azadiene)tricarbonyliron(0) complexes (*2*), which have π,π-coordination, complexation of the 1-azadiene with the metal causes an upfield shift of the protons in the 1-azadiene skeleton (see Chapter Five). Examination of the signal due to the N-C$\underline{H}_2$- protons in diacetyl-*n*-butylimine (*101*) shows that on complexation there is a downfield shift of δ 0.51. This suggests that bonding is *via* donation of the lone pair on the nitrogen atom to the metal, with a consequent deshielding of the nearby protons.

Bonding *via* σ,σ-coordination in (1,4-diazadiene)tricarbonyliron(0) complexes (*3*) was supported by investigations of the chemical shifts of complex (*104*) in ^{1}H and ^{13}C n.m.r. spectral studies[61].



(*105*) (*17*) (*104*)

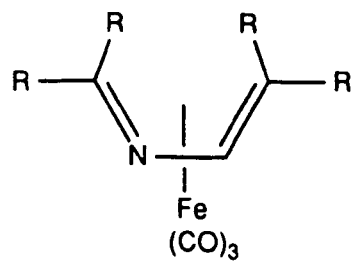
Attempts to synthesise (2,3-diazadiene)tricarbonyliron(0) complexes have been unsuccessful. Treatment of benzalazine (*106*) with $Fe_2(CO)_9$ (*17*) did not lead to the isolation of a tricarbonyliron(0) species. The only iron containing compound recovered apparently contained two -$Fe(CO)_3$ units and was tentatively assigned structure (*107*)[4].



(*106*) (*17*) (*107*)

Structure (*107*) was proposed on the basis of molecular weight determination, elemental analysis, and i.r. spectroscopy.

There are no reports in the literature of the preparation of (2-azadiene)tricarbonyliron(0) complexes (*108*).

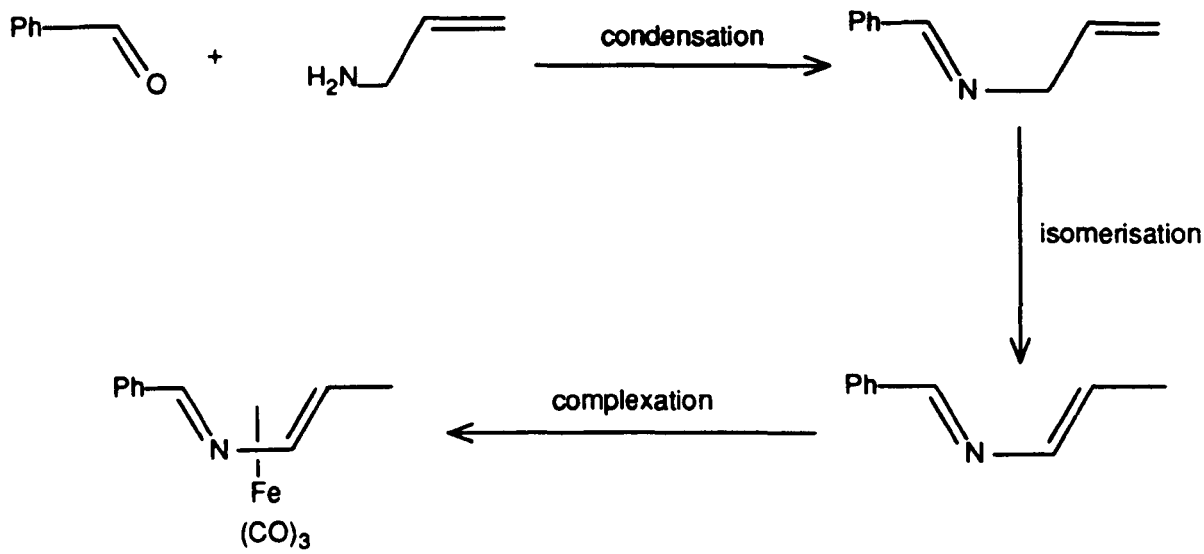


(*108*)

It was decided, therefore, to investigate the preparation of complexes of this type and examine the effect of the tricarbonyliron(0) moiety on the reactivity of the 2-azadiene ligand.

12. THE SYNTHESIS OF (2-AZADIENE)TRICARBONYLIRON(0) COMPLEXES (*109*)

2-Azadiene ligands were prepared by the isomerisation of a range of *N*-allylimines. This pathway is straightforward and uses readily-available starting materials. The approach to (2-azadiene)tricarbonyliron(0) complexes is outlined in Scheme 5:



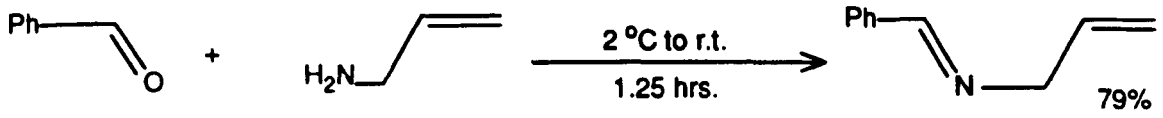
Scheme 5.

12.1 Preparation of 2-Azadienes.-

12.1.1 *N*-Allylimines.

N-(Benzylidene)-2-propen-1-amine (*109*) was formed by the condensation of benzaldehyde with allylamine [62]. Benzaldehyde was added dropwise to stirred allylamine at 2 °C. The reaction was allowed to warm to room temperature and stirred for 1.25 hours. The milky solution was dried over solid sodium hydroxide, and the organic phase dried over sodium carbonate and filtered. Distillation *in vacuo* gave the desired *N*-allylimine (*109*) as a pale yellow liquid (b.p. 61-69 °C, 0.2 mm Hg^{-1}) in 79% yield. The i.r. spectrum of imine (*109*) was dominated by a C = N stretch at 1 652 cm^{-1} and contained a C = C

stretch at 1 575 cm^{-1}. The ^1H n.m.r. spectrum contained a two-proton doublet (J 9 Hz) at δ 4.20 (N-C<u>H</u>$_2$-), two overlapping one-proton double doublets (J_{gem} 2 Hz, J_{cis} 12 Hz, and J_{trans} 19 Hz) at δ 5.20 (-CH = C<u>H</u>$_2$), a one-proton multiplet at δ 6.10 (-C<u>H</u> = CH$_2$), multiplets at δ 7.40 and δ 7.65 (three protons and two protons respectively, both -<u>Ph</u>), and a one-proton singlet at δ 8.25 (N = C<u>H</u>-Ph). The boiling point and the spectra were in good agreement with literature values[62,63].



(*109*)

A slightly modified procedure was then used to prepare a series of 4-aryl-substituted *N*-(benzylidene)-2-propen-1-amines. Allylamine was cooled to 2 °C in an ice-water cooling bath. A solution of the 4-aryl-substituted benzaldehyde in ethanol was added dropwise to the cooled amine. The reaction mixture was allowed to warm to room temperature and stirred until t.l.c. analysis indicated that the reaction was complete. The alcoholic reaction mixture was then concentrated *in vacuo*. Liquid *N*-allylimines were then distilled *in vacuo* to leave the desired imines as clear, colourless liquids. Solid imines were recrystallised from carbon tetrachloride to leave the desired imines as yellow crystals. The results are summarised in Table 7 overleaf.

Imines (*110*) and (*113*) have been previously reported in the literature but not fully characterised. Imines (*111*) and (*112*) are unreported. Imines (*109*)-(*113*) gave boiling or melting points, and ^1H n.m.r., i.r., and mass spectra which either agreed with literature data when available (see Table 7) or were entirely consistent with those expected. A satisfactory elemental analysis was obtained on the crystalline imine (*113*). The other imines (*110*), (*111*) and (*112*) were unstable liquids and decomposed overnight even if stored in a freezer. Elemental analyses could not, therefore, be obtained on these imines. They did, however, each give a satisfactory high resolution mass spectrum.

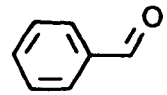
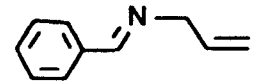
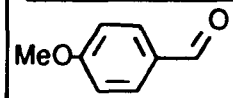
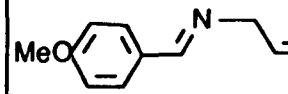
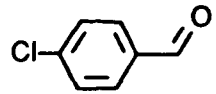
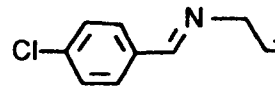
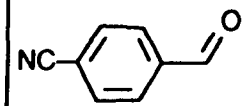
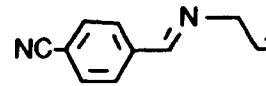
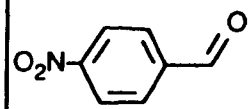
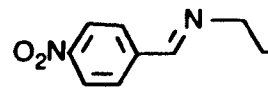
Aldehyde	Imine	Reaction time / hrs.	Yield of imine / %	Reference
	 (*109*)	1.25	79	62, 63, 64, 65
	 (*110*)	4.50	98	64, 65
	 (*111*)	2.50	96	
	 (*112*)	4.25	86	
	 (*113*)	2.75	99	65

Table 7: Formation of *N*-allylimines

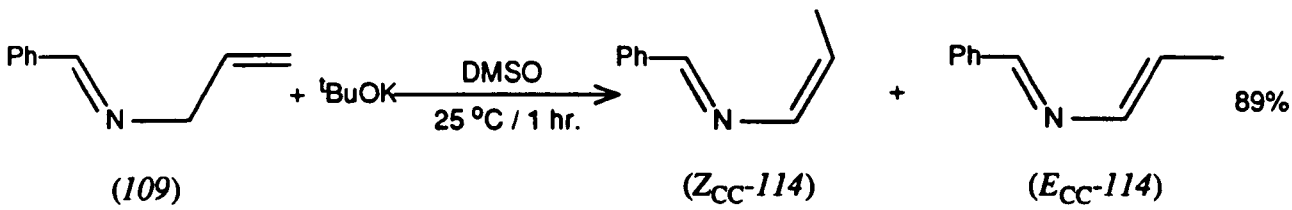
12.1.2 2-Azadienes.

The unsubstituted imine (*109*) was then isomerised to *N*-(benzylidene)-1-propen-1-amine (*114*) which contains the desired conjugated 2-azadiene system [63]. Imine (*109*) was suspended in DMSO and stirred at room temperature. Portionwise addition of 0.1 mole-equivalents of potassium *t*-butoxide caused the reaction mixture to become a dark brown colour. Stirring for 1 hour at 25 °C and then quenching with distilled water gave a light brown liquid. Extraction with ethyl acetate and washing with distilled water, followed by drying over sodium carbonate and concentration *in vacuo* gave a light brown oil. This oil was distilled *in vacuo* to furnish the desired 2-azadiene (*114*) as a pale yellow liquid (b.p. 60-65 °C; 0.2 mm Hg^{-1}) in 89% yield. The 2-azadiene was a mixture of E_{cc}- and Z_{cc}-isomers (approximately 2:1 by ^1H n.m.r. spectroscopy). The i.r. spectrum contained peaks at 1 645 (C = N) and 1 570 cm^{-1} (C = C) (*Z*-isomers) and 1 660 (C = N) and 1 610 (C = C) (*E*-isomer). The ^1H n.m.r. spectral data for compound (*114*) are given in Table 8.

Proton	*E*-isomer /δ	*Z*-isomer /δ
=CH-C<u>H</u>$_3$	1.90 (d, 3H, *J* 7 Hz)	2.05 (d, 3H, *J* 7 Hz)
=C<u>H</u>-CH$_3$	6.10 (dq, 1H, *J* 13 and 7 Hz)	5.45 (dq, 1H, *J* 10 and 7 Hz)
N-C<u>H</u>-CH-CH$_3$	6.75 (m, 1H)	6.75 (m, 1H)
<u>Ph-</u>	7.35-7.55 (m, 5H)	7.35-7.55 (m, 5H)
Ph-C<u>H</u>=N-	8.05 (s, 1H)	8.10 (s, 1H)

Table 8: ^1H n.m.r. chemical shifts of (*114*) in CCl_4

The boiling point and spectral data were in good agreement with literature values[63].

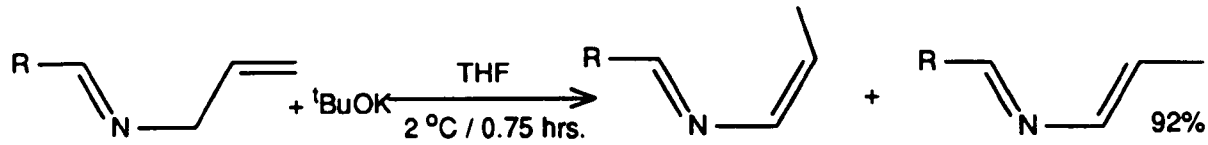


(*109*) (Z_{CC}-*114*) (E_{CC}-*114*)

1:2

Attempts to isomerise imines (*110*)-(*113*) under the same conditions were unsuccessful, resulting in intractable black gums. A modified procedure was thus employed[66].

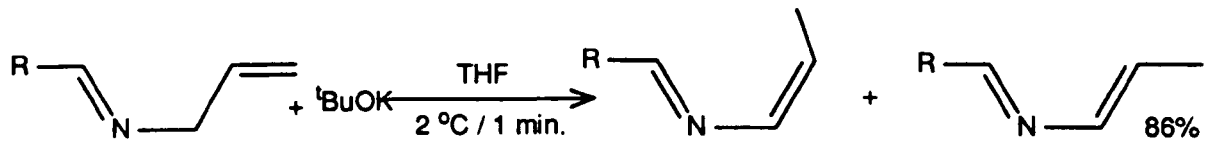
N-Allylimine (*110*) was diluted with THF and added to one mole-equivalent of ^{t}BuOK suspended in THF in an ice-water cooling bath. The reaction mixture immediately became bright orange. The reaction was stirred in the cooling bath until it became light brown (0.75 hours) and then quenched with distilled water. Extraction with ethyl acetate and then drying the organic phase over sodium carbonate and filtering gave a solution which was concentrated *in vacuo* to leave a light brown liquid. Distillation *in vacuo* gave the desired 2-azadiene (*115*) as a clear, colourless liquid (b.p. 83 °C; 0.2 mm Hg^{-1}) in 92% yield. 2-Azadiene (*115*) was a mixture of E_{cc}- and Z_{cc}-isomers (E_{cc}:Z_{cc} = 1:1.2 by ^{1}H n.m.r. spectroscopy). The colourless liquid was again unstable, decomposing overnight even if kept under nitrogen in a freezer, and a satisfactory elemental analysis could not be obtained. However, ^{1}H n.m.r., i.r. and high resolution mass spectra were all obtained and were in good agreement with literature values, where available[64,65,67].



(*110*) R = 4-MeO-C_6H_4- (Z_{CC}-*115*) (E_{CC}-*115*) R = 4-MeO-C_6H_4-

(1.2:1)

4-Chloro-phenyl substituted 2-azadiene (*116*) was prepared similarly. In this case, stirring a solution of *N*-allylimine (*111*) in THF with a suspension of 0.33 mole-equivalents of ^{t}BuOK in THF in an ice bath for only 1 minute was sufficient for a colour change (bright red to light brown). Work-up and distillation as before gave the desired 2-azadiene (*116*) as a clear, colourless liquid (b.p. 79 °C; 0.2mm Hg^{-1}) in 86% yield. The ^{1}H n.m.r., i.r. and high resolution mass spectra were all entirely consistent with structure (*116*):



(*111*) R = 4-Cl-C_6H_4- (Z_{CC}-*116*) (E_{CC}-*116*) R = 4-Cl-C_6H_4-

(1:1.7)

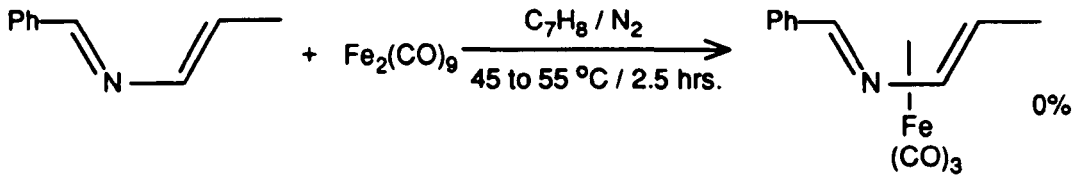
Attempts to isomerise imines (*112*) and (*113*) under the modified conditions were again unsuccessful and resulted in intractable brown gums.

12.2 Complexation of 2-Azadienes.-

Complexation reactions were carried out on mixtures of the E_{cc}- and Z_{cc}-isomers of the prepared 2-azadienes. The 'direct synthesis' procedure used successfully on 1-azadienes was employed[4].

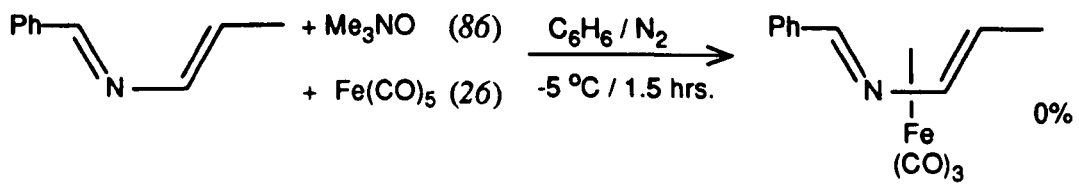
12.2.1 Complexation of unsubstituted 2-azadiene ligand (*114*).

Treatment of 2-azadiene (*114*) with $Fe_2(CO)_9$ (*17*) in toluene at 45 °C under a nitrogen atmosphere for 2.5 hours gave a dark red solution with no solid $Fe_2(CO)_9$ (*17*) remaining. Filtration and concentration *in vacuo* gave the starting material (*114*) as a brown liquid (98% recovery). Repeating the reaction at 55 °C again resulted in the recovery of starting material (*114*) (84% recovery). In neither case could any peaks due to complexed material (*117*) be detected in the ^1H n.m.r. spectrum of the reaction mixture.



(*114*) (*17*) (*117*)

An alternative, very mild complexation procedure was used[68]. 2-Azadiene (*114*) and an excess of trimethyloxamine (*86*) were dissolved in benzene. Treatment with $Fe(CO)_5$ (*26*) at -5 °C under a nitrogen atmosphere for 1.5 hours gave a red-brown solution. Filtration and concentration *in vacuo* gave the starting ligand (*114*) as a brown liquid (77% recovery).



(*114*) (*117*)

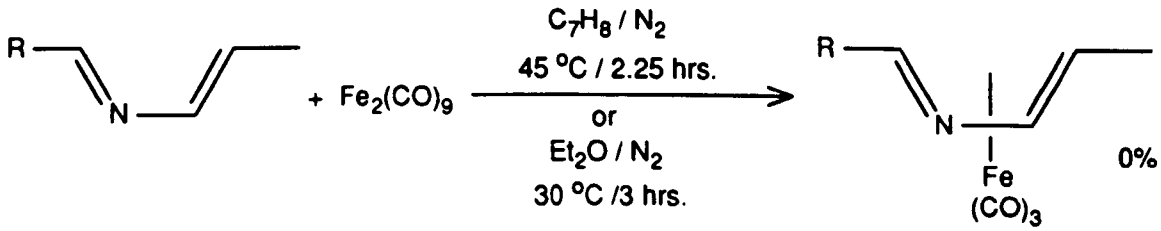
Finally, complexation using $Fe_2(CO)_9$ (*17*) under mild conditions was used. 2-Azadiene (*114*) was dissolved in diethyl ether and $Fe_2(CO)_9$ (*17*) added. Stirring under a nitrogen atmosphere at room temperature for 0.5 hours and then at 30 °C for 2.5 hours gave a dark brown liquid. Filtration and concentration *in vacuo* gave a dark red-brown oil. The oil proved to be too unstable for an ^1H n.m.r. spectrum to be obtained and even after repeated

filtrations through alumina the signals were very broad. The i.r. spectrum, however, contained two broad bands in the region 2 020 to 1 970 cm^{-1}. This is the characteristic region of C≡O stretches in organic iron carbonyl complexes[69]. The result of this reaction suggests that a complex is formed but that it is highly unstable.

The stability of (1-azadiene)tricarbonyliron(0) complexes (*2*) is known to be increased if the electrons donated to the ligand by the iron d-orbitals can be delocalised into an aromatic ring[7]. The incorporation of an electron-withdrawing substitutent into the phenyl ring of 2-azadiene (*114*) would, therefore, be expected to stabilize its iron carbonyl complexes by increasing the delocalisation of electrons from the C=N-C=C chain.

It was decided, therefore, to complex 2-azadiene (*116*), bearing the net electron-withdrawing substituent -Cl. 2-Azadiene (*116*) was dissolved in toluene and $Fe_2(CO)_9$ (*17*) added. The reaction mixture was stirred at 45 °C under a nitrogen atmosphere for 2.25 hours. Filtration and concentration *in vacuo* led to the recovery of starting ligand *(116)* in 70% yield.

Repeating the low temperature reaction in diethyl ether for 3 hours, followed by filtration and concentration *in vacuo* again led only to the recovery of starting ligand (*116*), this time in 74% yield. No trace of any complex was detectable in the ^1H n.m.r. or i.r. spectra.

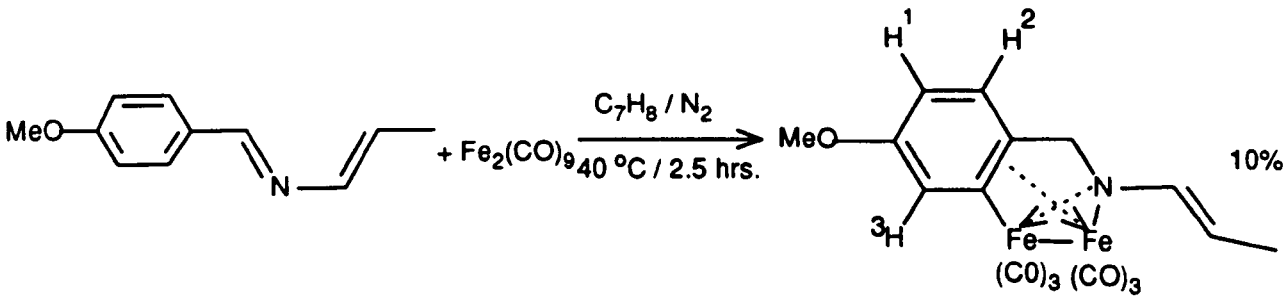


(*116*) R = 4-Cl-C_6H_4- (*17*) (*117*) R = 4-Cl-C_6H_4-

12.2.2 Complexation of *N*-(4-methoxybenzylidene)-1-propen-1-amine (*115*).

The other available 2-azadiene (*115*), bearing a 4-methoxy phenyl group, and one

mole-equivalent of $Fe_2(CO)_9$ (*17*) were stirred in toluene at 40 °C for 2.5 hours under a nitrogen atmosphere. The dark brown reaction mixture was filtered and concentrated *in vacuo* to leave a dark red solid. This solid was crystallised from di-*n*-butylether to leave ruby red prisms, melting point 102-104 °C. The prisms were assigned structure (*118*) on the basis of the spectroscopic data.

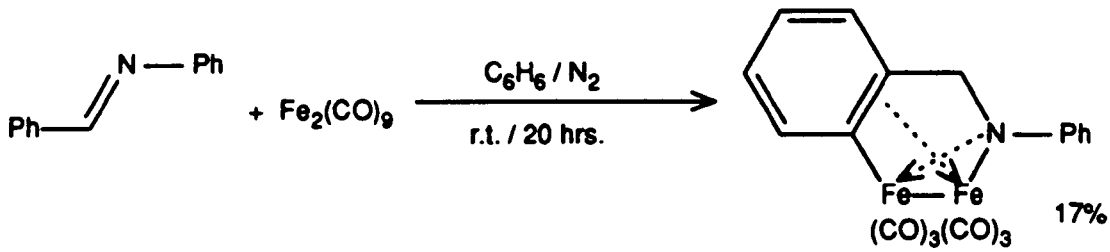


(*115*) (*17*) (*118*)

The mass spectrum suggested the presence of two -$Fe(CO)_3$ moieties. There was a molecular ion (455, 19%) and then peaks at 427 (24%), 399 (100%), 371 (78%), 343 (63%), 315 (35%) and 287 (39%) due to the successive loss of six C≡O groups. The i.r. spectrum contained four strong C≡O absorptions at 2 070, 2 035, 1 997 and 1 990 cm^{-1} and an absorption at 1 597 cm^{-1}assigned to the carbon-carbon double bond. The 400 MHz ^1H n.m.r. spectrum contained a three-proton double doublet at δ 1.54 (*J* 1.5 and 6.7 Hz) (=CH-C$\underline{H}_3$), a three-proton singlet at δ 3.77 (-OC$\underline{H}_3$), a two-proton singlet at δ 3.98 (=CH-N-C$\underline{H}_2$-), a one-proton double quartet at δ 4.79 (*J* 13.5 and 6.7 Hz) (Me-CH=), a one-proton double quartet at δ 5.83 (*J* 13.4 and 1.5 Hz) (N-C$\underline{H}$=CH-), a one-proton double doublet at δ 6.92 (*J* 2.4 and 8.8 Hz) ($\underline{H}^1$), and one-proton doublets at δ 7.26 (*J* 2.4 Hz) ($\underline{H}^3$) and δ 7.53 (*J* 8.8 Hz) ($\underline{H}^2$). The elemental analysis was consistent with the assigned structure.

Support for this structural assignment is provided by the outcome of complexation of *N*-benzylideneaniline (*119*)[70]. The reaction yielded a complex which was identified as the

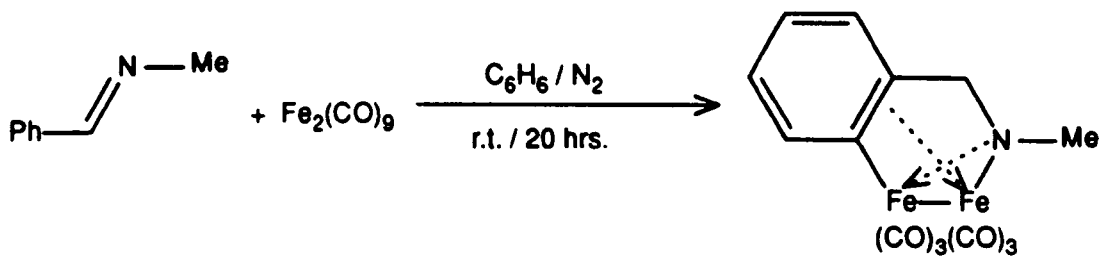
dimetallic species (*120*) on the basis of the following evidence.



(*119*) (*17*) (*120*)

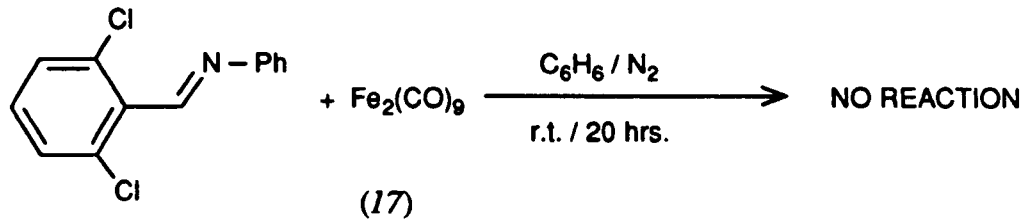
The mass spectrum of complex (*120*) showed the characteristic loss of six successive C≡O groups and the i.r. spectrum contained four strong C≡O absorptions (2 062, 2 024, 1 993 and 1 982 cm^{-1}). In addition to the spectroscopic studies a number of chemical studies were also carried out to elucidate the structure[70]:

(i) Involvement of the *N*-aryl substituents was discounted by the formation of the analogous complex *(121)* from benzylidenemethylamine (*122*):



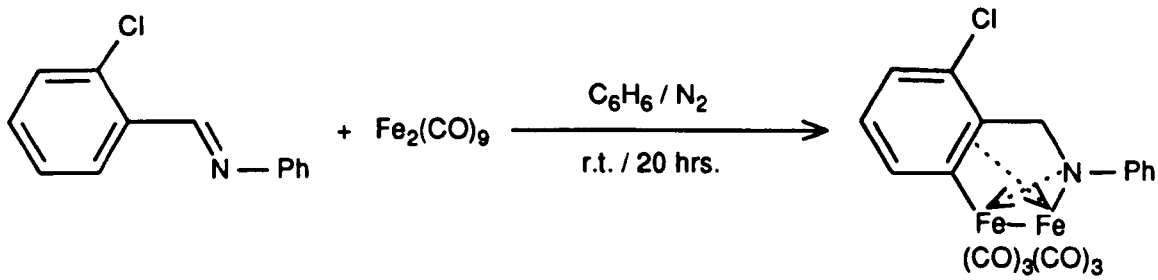
(*122*) (*17*) (*121*)

(ii) Replacing the 2,6-phenyl hydrogens in the aromatic ring with chlorine atoms prevented complexation and, therefore, implicated the 2,6-phenyl hydrogens as playing a role in the formation of the complex:



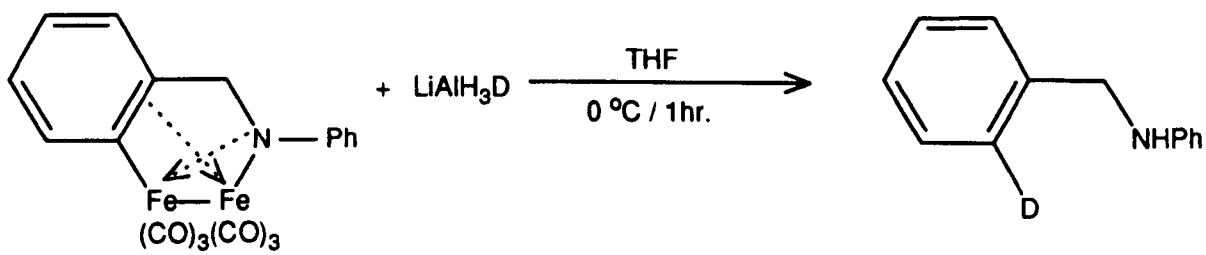
(*17*)

Replacement of only one 2-phenyl hydrogen atom [as in imine (*123*)] still allowed complexation to take place:



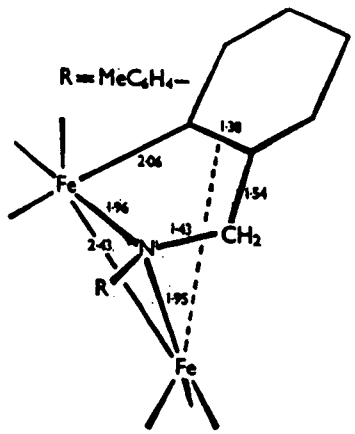
(*123*) (*17*)

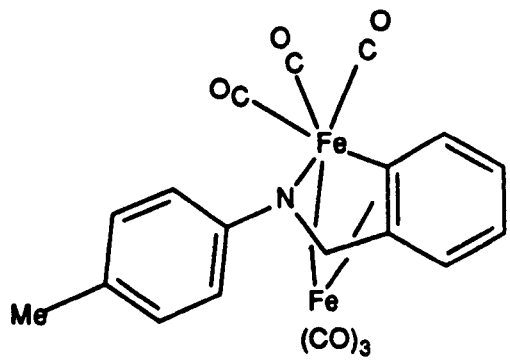
(iii) Reduction of (*120*) with lithium aluminium deuteride gave secondary amine (*124*):



(*120*) (*124*)

The stucture of these complexes has been proven by X-ray crystallography on complex (*125*)[71].

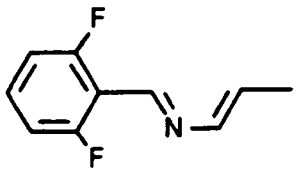




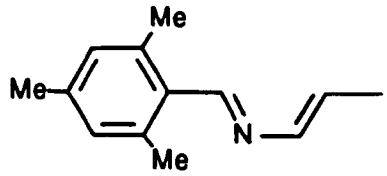
(*125*)

12.2.3 Preparation of hindered 2-azadienes.

The presence of a 2-phenyl hydrogen in the aromatic ring is essential for the formation of the $Fe_2(CO)_6$ complexes described above. It was postulated that if 2-azadienes were synthesised which did not have 2-phenyl hydrogen atoms, then (2-azadiene)tricarbonyliron(0) complexes might, under suitable conditions, be formed on complexation. With this in mind, the preparation of two 'hindered' 2-azadienes (*126*) and (*127*) was undertaken.



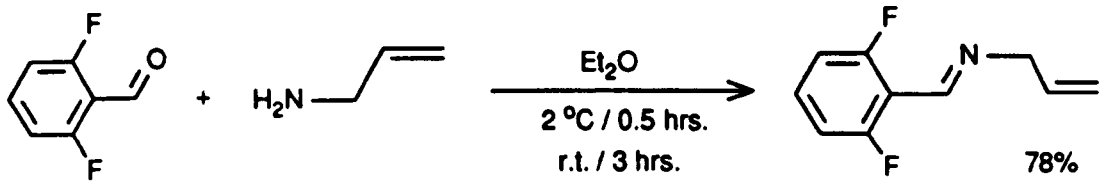
(*126*)



(*127*)

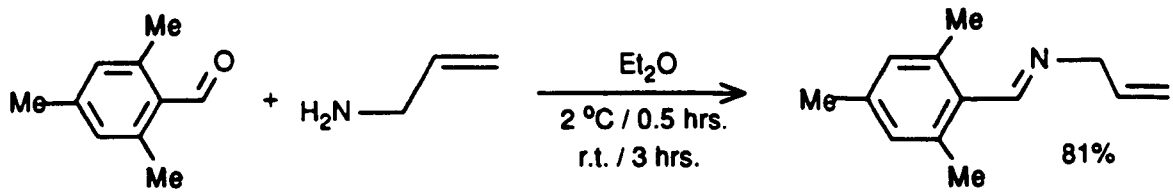
2,6-Difluorobenzaldehyde was stirred in diethyl ether in an ice-water cooling bath. *N*-Allylamine was added dropwise over 2 minutes. The resulting solution was stirred in the cooling bath for 0.5 hours and then at room temperature for 3 hours. Dilution with diethyl ether, drying over sodium carbonate and then filtering left a pale yellow liquid which was concentrated *in vacuo* and then distilled under reduced pressure to leave

N-allylimine (*128*) as a clear, colourless liquid (b.p. 56-58 °C; 0.2 mm Hg^{-1}) in 78% yield. The i.r. spectrum contained strong absorptions at 1 650 (C=N), 1 625 (C=C), and 1 240 cm^{-1} (C-F). The ^1H n.m.r. spectrum contained a two proton doublet at δ 4.33 (*J* 5 Hz) (=N-C<u>H</u>$_2$-), two overlapping one-proton double doublets (J_{gem} 2 Hz, J_{cis} 12 Hz, and J_{trans} 19 Hz) at δ 5.33 (-CH=C<u>H</u>$_2$), a one-proton multiplet at δ 6.10 (H_2C=C<u>H</u>-), multiplets at δ 6.95 and δ 7.35 (two- and one-proton, both <u>Ar</u>-), and a one-proton singlet at δ 8.53 (-N=C<u>H</u>-Ph). The liquid was too unstable to give a satisfactory elemental analysis but a satisfactory high resolution mass spectrum was obtained.



(*128*)

The same procedure was used on 2,4,6-trimethylbenzaldehyde to produce *N*-allylimine (*129*) as a clear, colourless liquid (b.p. 118 °C; 0.2 mm Hg^{-1}) in 81% yield. Again the ^1H n.m.r., i.r. and high resolution mass spectra were all consistant with the structure of imine (*129*).



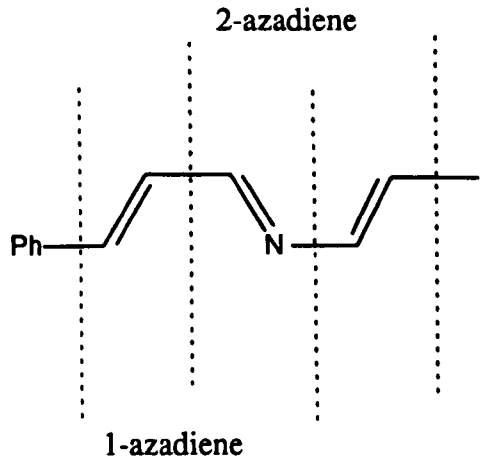
(*129*)

N-(2,6-Difluorobenzylidene)-1-propen-1-amine (*128*) was diluted with THF and added to 0.33 mole-equivalents of ^{t}BuOK in THF in an ice-water cooling bath. The resulting bright red mixture became brown after 1 minute. The reaction was quenched wth distilled water and extracted with ethyl acetate. The organic phase was dried over sodium carbonate, filtered, and concentrated *in vacuo* to leave an intractable brown gum.

Treatment of *N*-(2,4,6-trimethylbenzylidene)-1-propen-1-amine (*129*) with 0.25 mole-equivalents of ^{t}BuOK for 2 minutes in the same way as above again unfortunately resulted in the isolation of an intractable brown gum.

12.3 Complexation of 1-Phenyl-4-azaheptatriene (*130*).-

1-Phenyl-4-azaheptatriene (*130*) contains both a 1-azadiene and a 2-azadiene unit:

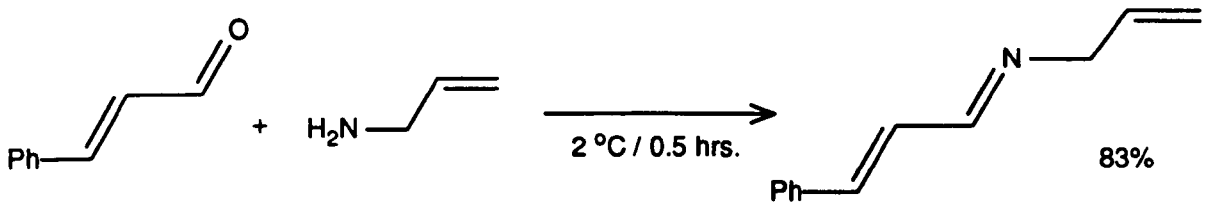


(*130*)

It was of interest, therefore, to prepare the tricarbonyliron(0) complex of this compound to determine the mode of bonding in the product.

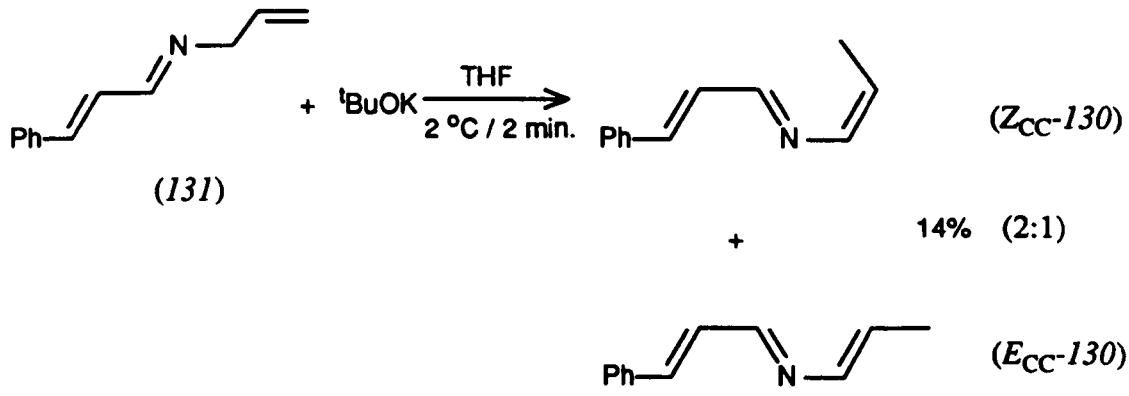
N-Allylamine was stirred in an ice-water cooling bath and cinnamaldehyde (*25*) added dropwise over 5 minutes. After 0.5 hours the reaction was diluted with diethyl ether, dried over magnesium sulphate and filtered. Concentration *in vacuo* and then distillation under reduced pressure left the desired *N*-allylimine (*131*) as a pale yellow liquid (b.p. 116 °C; 0.2 mm Hg^{-1}) in 83% yield. The i.r. spectrum of this liquid contained strong absorptions at 1 640 (C=N), 1 605 (C=C) and 1 590 cm^{-1} (C=C). The ^{1}H n.m.r. spectrum contained a two-proton doublet at δ 4.15 (*J* 6 Hz) (N-C$\underline{H}_2$-CH=), two overlapping one-proton double doublets at δ 5.20 (J_{gem} 2 Hz, J_{cis} 12 Hz, and J_{trans} 17 Hz) ($\underline{H}_2$C=CH-CH$_2$-), a one-proton multiplet at δ 6.07 (H_2C=C$\underline{H}$-CH$_2$), a two-proton doublet at δ 6.98 (*J* 6 Hz) (Ph-C$\underline{H}$=C$\underline{H}$-), a five-proton multiplet from 7.35-7.55 ($\underline{Ph}$-), and a one-proton doublet at δ 8.02 (*J* 6 Hz)

(-N=C<u>H</u>-CH=). The liquid was too unstable to give a satisfactory elemental analysis but the composition was confirmed by high resolution mass spectroscopy.

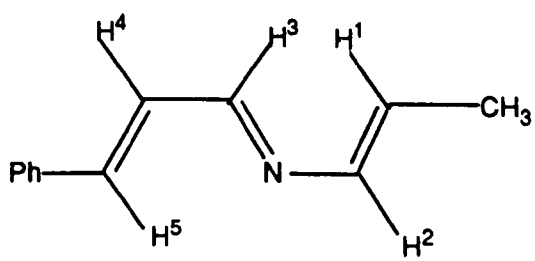


(*25*) (*131*)

N-Allylimine (*131*) in THF was then added to a stirred suspension of one mole-equivalent of ^{t}BuOK in THF in an ice-water cooling bath. The reaction was stirred for 2 minutes (by which time the colour had changed from purple to brown) and then quenched with distilled water. Extraction with ethyl acetate, drying over sodium carbonate and filtering left a yellow solution that was concentrated and distilled *in vacuo* to present the desired heptatriene (*130*) as a pale yellow liquid (b.p. 124 °C; 0.3 mm Hg^{-1}) in 14% yield. The heptatriene (*130*) was a mixture of Z_{cc}- and E_{cc}-isomers (approximately 2:1 by ^{1}H n.m.r. spectroscopy). The i.r. spectrum contained absorptions at 1 636 (C=N), 1 616 (C=C) and 1 577 cm^{-1} (C=C). The ^{1}H n.m.r. spectrum contained: (E_{cc}-isomer) a three-proton doublet at δ 1.84 (*J* 7 Hz) (-C<u>H</u>$_3$), a one-proton double quartet at δ 6.15 (*J* 7 and 17 Hz) (CH_3-C<u>H</u>=CH-), a one-proton doublet at δ 6.75 (*J* 17 Hz) (CH_3-CH=C<u>H</u>-N), a two-proton multiplet at δ 7.07 (Ph-C<u>H</u>=C<u>H</u>-), a broad five-proton multiplet from δ 7.35 to 7.65 (<u>Ph</u>-), and a one-proton doublet at δ 8.05 (*J* 6 Hz) (-N=C<u>H</u>-); (Z-cc-isomer) a three-proton doublet at δ 2.05 (*J* 7 Hz) (-C<u>H</u>$_3$), a one-proton double quartet at δ 5.50 (*J* 7 and 12 Hz) (CH_3-C<u>H</u>=CH-), a one-proton doublet at δ 6.75 (*J* 12 Hz) (CH_3-CH=C<u>H</u>-N), a two-proton multiplet at δ 7.07 (Ph-C<u>H</u>=C<u>H</u>-), a broad multiplet from δ 7.35 to 7.65 (<u>Ph</u>-), and a one-proton doublet at δ 8.05 (*J* 6 Hz) (-N=C<u>H</u>-). Once again the liquid was too unstable for an elemental analysis but composition was confirmed by a high resolution mass spectrum.

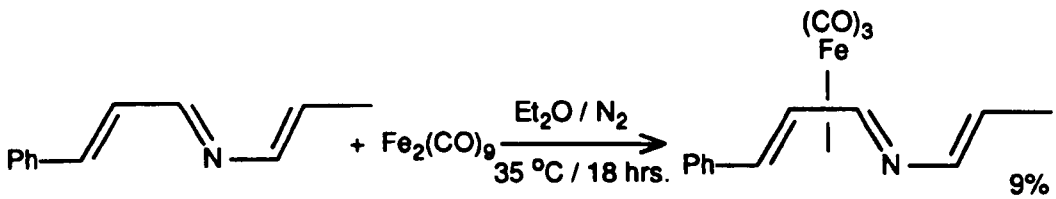


Complexation of heptatriene (*130*) was then examined. Heptatriene (*130*) and $Fe_2(CO)_9$ (*17*) were stirred in diethyl ether at reflux under a nitrogen atmosphere for 18 hours. Filtration through alumina and concentration *in vacuo*, followed by chromatography gave orange crystals. The i.r. spectrum of these crystals contained three strong C≡O absorptions at 2 055, 1 998 and 1 982 cm^{-1} confirming that the crystals were a tricarbonyliron complex. The ^1H n.m.r. spectrum contained a three-proton doublet at δ 1.78 (*J* 7 Hz) (-C<u>H</u>$_3$), a one-proton doublet at δ 3.25 (*J* 17 Hz) (Ph-C<u>H</u>=), a one-proton double doublet at δ 5.55 (*J* 17 and 11 Hz) (Ph-CH=C<u>H</u>-), a one-proton double quartet at δ 6.03 (*J* 7 and 17 Hz) (CH_3-C<u>H</u>=), a one-proton doublet at δ 6.75 (*J* 17 Hz) (CH_3-CH=C<u>H</u>-N), and a six proton multiplet from δ 7.25 to 7.35 (<u>Ph</u>- and N=C<u>H</u>-). Examination of the chemical shifts of the protons in the heptatriene skeleton (*130*) revealed that the protons of the 2-azadiene skeleton (H^1 and H^2) are not shifted.



(*130*)

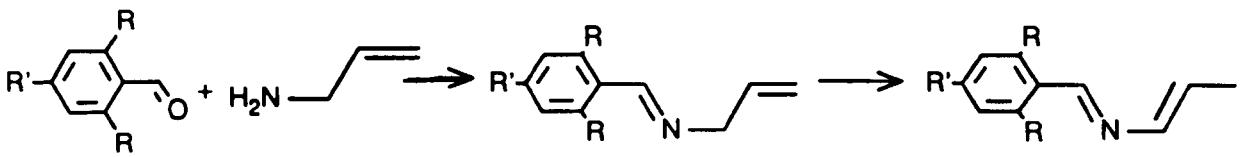
The protons of the 1-azadiene skeleton, however, are shifted (H^3 $\Delta\delta$ 0.8, H^4 $\Delta\delta$ 1.52, and H^5 $\Delta\delta$ 3.82). The pattern and magnitude of the chemical shifts is consistent with the shifts recorded on complexation of 1-azadiene ligands, *e.g.* cinnamaldehydeanil (*5*) (See Chapter Five).



(*130*) (*132*)

13. SUMMARY OF THE PREPARATION OF (2-AZADIENE)-TRICARBONYLIRON(0) COMPLEXES (*108*)

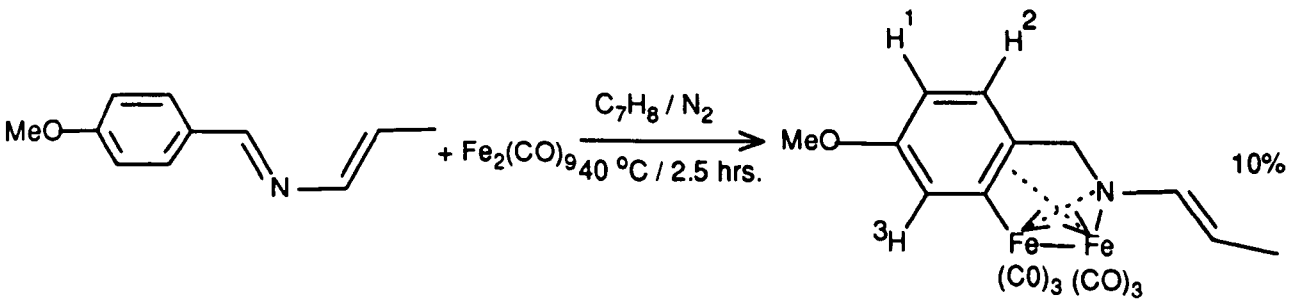
(2-Azadiene)tricarbonyliron(0) complexes (*108*) have never been reported. A series of unsaturated imines has been prepared [R=H,R'=H (*109*), CN (*112*), Cl (*111*), OMe (*110*), NO_2 (*113*); R=R'=Me (*129*); R=F, R'=H (*128*)] some of which [(*109*), (*111*), (*110*)] could be isomerised to a 2-azadiene ligand.



R = H, R' = H (*109*) 89%
R = H, R' = CN (*112*) 86%
R = H, R' = Cl (*111*) 96%
R = H, R' = OMe (*110*) 98%
R = H, R' = NO_2 (*113*) 99%
R = R' = Me (*129*) 81%
R = F, R' = H (*128*) 78%

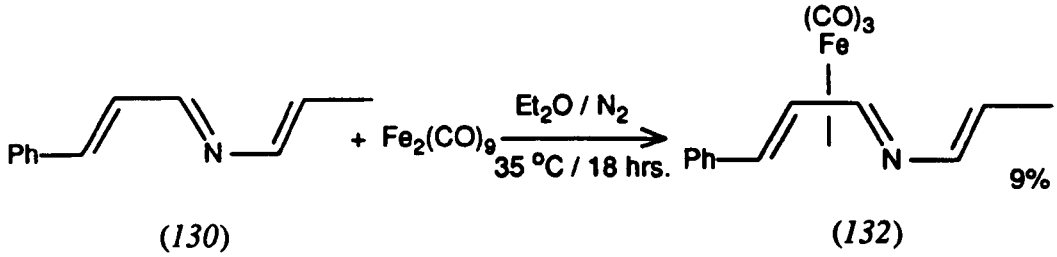
R = R' = H (*114*) 89%
R = H, R' = Cl (*117*) 86%
R = H, R' = OMe (*115*) 92%

Complexation of these 2-azadienes using $Fe_2(CO)_9$ (*17*) or $Fe(CO)_5$ (*26*) did not produce a tricarbonyliron(0) complex. Complexation of 2-azadiene (*115*) (R=H, R'=OMe), with $Fe_2(CO)_9$ (*17*), however, produced a $Fe_2(CO)_6$ containing compound (*118*):



(*115*) (*17*) (*118*)

1-Phenyl-4-azaheptatriene (*130*), which contained both a 1- and 2-azadiene system could be complexed to form only a (1-azadiene)tricarbonyliron(0) complex (*132*). No sign of the (2-azadiene)tricarbonyliron(0) complex could be detected.



(*130*) (*132*)

Thus, (2-azadiene)tricarbonyliron(0) complexes (*109*) remain elusive.

EXPERIMENTAL

General Experimental

Reactions under nitrogen were performed using standard vacuum line and Schlenk tube techniques[72].

Diethyl ether was dried over sodium wire.

Tetrahydrofuran was dried over sodium wire and distilled.

Acetone was shaken with silver nitrate and sodium hydroxide solutions, filtered, dried over calcium sulphate, and distilled[73].

Maleic anhydride and *potassium* t-*butoxide* were purified by sublimation.

60-80 Petroleum ether was distilled, and refers to the fraction boiling between 60 and 80 °C.

Filtration through *alumina* used deactivated (Grade V) basic alumina.

Column chromatography was performed using Merck Kieselgel 60 (230-400 mesh) silica.

I.r. spectra were recorded on a Perkin Elmer 580B or 1720X instrument and calibrated against a polystyrene standard.

N.m.r. spectra were recorded on a Perkin Elmer R34 (220 MHz, ^1H) or Bruker WH400 (400 MHz, ^1H) instrument, using tetramethylsilane as internal standard.

Mass spectra were recorded on a Kratos MS 80 instrument at 70 eV, using chemical ionisation (C.I.) (NH_3), electron ionisation (E.I.), and fast atom bombardment (FAB) (matrix: *m*-nitrobenzyl alcohol) techniques.

Elemental analyses were performed by MEDAC Ltd, Brunel University Chemistry Department.

Melting points were determined using Gallenkamp MFB-595 melting point apparatus, and are uncorrected.

Cinnamaldehydeanil (*5*).-

Aniline (4.65 g, 49.9 mmol) was added dropwise over 1 minute to rapidly stirred cinnamaldehyde (*25*) (6.61 g, 50.0 mmol) at 2 °C. This led to the immediate precipitation of a yellow solid which was collected by filtration, dissolved in diethyl ether and dried over magnesium sulphate. Filtration, followed by concentration *in vacuo* provided yellow crystals which were recrystallised from ethanol and dried *in vacuo* to yield the title compound (*5*) as pale yellow crystals (9.43 g, 91%), m.p. 109-110 °C [lit.[74] 109 °C]; $\upsilon_{max.}$ (nujol) 1 620 (C=N) and 1 570 cm^{-1} (C=C) [lit.[4] (nujol) 1 621 and 1 571 cm^{-1}]; δ_H (220 MHz; $CDCl_3$) 7.20-7.65 (12H, m, 2 x Ph and Ph-CH=CH-) and 8.30 (1H, m, Ph-N=CH-) [lit.[4] (CCl_4) 7.00-7.45 (12H, m), and 8.12 (1H, q)]; *m/z* (E.I.) 206 (M^+, 100%).

Di-iron enneacarbonyl (*17*).-

Iron pentacarbonyl (*26*) (156.50 g, 0.80 mol) was diluted with acetic acid (450 ml) and the resulting orange solution irradiated with ultraviolet light for 7.5 hours under a nitrogen atmosphere. The resulting orange crystals were harvested by filtration and washed, first with ethanol (3 x 250 ml) and then with diethyl ether (3 x 200 ml). After drying the crystals *in vacuo* in the dark the title compound (*17*) was furnished as golden-yellow flakes (69.43 g, 48%), m.p. 112 °C (dec.) [lit.[75] 100-120 °C (dec.)]; $\upsilon_{max.}$ (nujol) 2 085 (CO), 2 040 (CO), and 1 830 cm^{-1} [lit.[19] 2 080, 2 034, and 1 828 cm^{-1}].

(Cinnamaldehydeanil)tricarbonyliron(0) (*4*).-

Cinnamaldehydeanil (*5*) (0.74 g, 3.6 mmol) and di-iron enneacarbonyl (*17*) (1.30 g, 3.6 mmol) were suspended in toluene (10 ml) and heated at 40 °C for 2.5 hours under a

nitrogen atmosphere. The resulting dark red mixture was filtered, and concentrated *in vacuo* to furnish a dark red solid. This solid was recrystallised twice from *n*-heptane and the crop harvested by filtration. Drying *in vacuo* gave the title compound (*4*) as ruby red needles (0.52 g, 42%), m.p. 108-109 °C [lit.[4] 108.5 - 110.5 °C (dec.)]; $\upsilon_{max.}$ (nujol) 2 050 (CO), 1 985 (CO), and 1 950 cm^{-1} (CO) [lit.[4] (nujol) 2 060, 1 998, and 1 990 cm^{-1}]; δ_H (220 MHz; $CDCl_3$) 3.55 (1H, d, *J* 10 Hz, Ph-C<u>H</u>=), 5.75 (1H, dd, *J* 10 and 2 Hz, Ph-CH=C<u>H</u>-), and 6.95-7.40 (11H, broad m, 2 x <u>Ph</u>- and N=C<u>H</u>-) [lit.[4] (CCl_4) 3.35 (1H, d), 5.65 (1H, dd), and 6.70-7.40 (11H, m) *n.b.* no coupling constants given]. *m/z* (FAB) 347 (M^+, 27%), 319 (M^+-CO, 53%), 291 (M^+-2CO, 100%), and 263 (M^+-3CO, 49%).

(Cinnamaldehydeanil)tricarbonyliron(0) (*4*) using ultrasound.-

An ultrasound cleaning bath was filled with fresh tap water to a level 1.0 cm below the rim. Decon 1000 (soap solution, 5 ml) was added. The bath was switched on and allowed to run for 5 minutes. Meanwhile, a Schlenk tube was charged with cinnamaldehydeanil (*5*) (0.24 g, 1.16 mmol), di-iron enneacarbonyl (*17*) (0.49 g, 1.42 mmol) and benzene (10 ml). The Schlenk tube was sealed with a septum containing a thermometer, the bulb of which was immersed in the reaction mixture. The Schlenk tube was degassed and then subjected to a nitrogen atmosphere. By means of fixed clamps the Schlenk tube was positioned in the centre of the bath and immersed to a depth of 3.0 cm. The reaction mixture was sonicated in the bath for 2.5 hours, by which time no solid di-iron enneacarbonyl (*17*) remained and the temperature of the reaction mixture had risen from 20.5 to 40.0 °C. The dark red solution was concentrated *in vacuo* to leave a gum. This gum was dissolved in diethyl ether, filtered through alumina, and the filtrate concentrated *in vacuo* to leave a dark red solid. Chromatography on silica using 40-60 petroleum ether: diethyl ether (7:1) provided the title compound (*4*) as ruby red needles (0.32 g, 82%), m.p. 108-110 °C [lit.[4] 108.5-110.5 °C (dec.)]; $\upsilon_{max.}$ (nujol) 2 055 (CO), 1 990 (CO), and 1 960 cm^{-1} [lit.[4] (nujol) 2 060, 1 998, and 1 990 cm^{-1}]; δ_H (220 MHz; $CDCl_3$) 3.41 (1H, d, *J* 10

Hz, Ph-C<u>H</u>=), 5.73 (1H, dd, *J* 10 and 2 Hz, Ph-CH=C<u>H</u>-), and 6.95-7.35 (11H, broad m, 2 x <u>Ph</u>- and N=C<u>H</u>-) [lit.[4] (CCl_4) 3.35 (1H, d), 5.65 (1H, dd), and 6.70-7.40 (11H, m)].

(Benzylideneacetone)tricarbonyliron(0) (*29*).-

Benzylideneacetone (*40*) (0.82 g, 5.61 mmol) and di-iron enneacarbonyl (*17*) (3.35g, 9.21 mmol) were suspended in toluene (15 ml) and heated at 60 °C for 5.5 hours under a nitrogen atmosphere. The reaction mixture was allowed to cool to room temperature and then filtered through alumina. The residue was washed with diethyl ether (2 x 10 ml). The combined filtrates were concentrated *in vacuo* to leave a red-brown solid. This solid was chromatographed on silica using 40-60 petroleum ether:diethyl ether (20:1) as eluent. An orange-red band was collected and concentrated *in vacuo* to leave a red solid which was recrystallised from hexane to give the title compound (*29*) as orange crystals (0.95 g, 56%), m.p. 88-90 °C [lit.[6] 88-90 °C]; $\upsilon_{max.}$ ($CHCl_3$) 2 060 (CO), 2 010 (CO), and 1 990 cm^{-1} (CO) [lit.[6] (cyclohexane) 2 065, 2 005, and 1 985 cm^{-1}]; δ_H (220 MHz; $CDCl_3$) 2.55 (3H, s, -C<u>H</u>$_3$), 3.13 (1H, d, *J* 9 Hz, Ph-C<u>H</u>=), 6.08 (1H, d, *J* 9 Hz, Ph-CH=C<u>H</u>-), and 7.30-7.40 (5H, m, -<u>Ph</u>) [lit.[6] ($CDCl_3$) 2.50 (3H, s), 3.10 (1H, d, *J* 9 Hz), and 6.02 (1H, d, *J* 9 Hz) *n.b.* signal due to phenyl protons not given].

Typical transfer reaction- synthesis of (cinnamaldehydeanil)tricarbonyliron(0) (*4*).-

(Benzylideneacetone)tricarbonyliron(0) (*29*) (0.13g, 0.42 mmol) and cinnamaldehydeanil (*5*) (0.09 g, 0.43 mmol) were suspended in toluene (10 ml) and stirred at 85 °C under a nitrogen atmosphere for 84 hours after which time t.l.c. (5% dichloromethane - 10% ethyl acetate - 85% 40-60 petroleum ether) indicated that no starting complex (*29*) remained. The brown reaction mixture was allowed to cool, filtered through alumina, and then concentrated *in vacuo* to leave an orange solid. This solid was chromatographed on silica

using 40-60 petroleum ether:ethyl acetate (19:1) as eluent. The orange band was collected and concentrated *in vacuo* to leave the title complex (*4*) as red needles (0.09 g, 62%), m.p. 108-109 °C [lit.[4] 108.5-110.5 °C (dec.)]; $\upsilon_{max.}$ (nujol) 2 062 (CO), 1 988 (CO), and 1 955 cm^{-1} (CO) [lit.[4] (nujol) 2 060, 1 998, and 1 990 cm^{-1}]; δ_H (220 MHz; $CDCl_3$) 3.33 (1H, d, *J* 10 Hz, Ph-C<u>H</u>=), 5.75 (1H, dd, *J* 2 and 10 Hz, Ph-CH=C<u>H</u>-), and 6.95-7.40 (11 H, broad m, 2 x <u>Ph</u>- and -N=C<u>H</u>-) [lit.[4] (CCl_4) 3.35 (1H, d), 5.65 (1H, dd), and 6.70-7.40 (11H, m)]; *m/z* (FAB) 347 (M^+, 23%), 319 (M^+-CO, 58%), 291 (M^+-2CO, 100%), and 263 (M^+-3CO, 50%).

(Cinnamaldehyde)tricarbonyliron(0) (*42*).-

Cinnamaldehyde (*25*) (0.96 g, 7.26 mmol) and di-iron enneacarbonyl (*17*) (5.28 g, 14.5 mmol) were suspended in diethyl ether (30 ml) and stirred under a nitrogen atmosphere at 37 °C for 24 hours. The reaction mixture was allowed to cool for 0.5 hours and then filtered through an alumina column. Any residues were washed with diethyl ether (2 x 10 ml). The combined filtrates were concentrated *in vacuo* to leave an orange-red solid. Re-crystallisation from *n*-hexane furnished the title compound (*42*) as thermally-unstable brick-red needles (1.03 g, 52%), $\upsilon_{max.}$ ($CHCl_3$) 2 075 (CO), 2 017 (CO), and 1 996 cm^{-1} (CO) [lit.[6] (*n*-hexane) 2 073, 2 015, and 1 994 cm^{-1}]; δ_H (220 MHz; $CDCl_3$) 3.29 (1H, d, *J* 9 Hz, Ph-C<u>H</u>=), 6.17 (1H, d, *J* 9 Hz, Ph-CH=C<u>H</u>-), 7.32 (5H, m, -<u>Ph</u>), and 7.65 (1H, s, -C<u>H</u>=O) [lit.[6] (CCl_4) 3.13 (1H, d, *J* 6 Hz), 5.95 (1H, d), and 7.52 (1H, s) *n.b.* no signal due to -Ph region quoted]; *m/z* (C.I.) 272 (M+1, 15%), and 133 (M-$Fe(CO)_3$, 100%).

(1,4-Diphenylbutadiene)tricarbonyliron(0) (*43*).-

1,4-Diphenylbutadiene (*41*) (0.77 g, 3.73 mmol) and di-iron enneacarbonyl (*17*) (3.06 g, 8.40 mmol) were suspended in toluene (20 ml) and stirred at 45 °C for 24 hours under a nitrogen atmosphere. The dark green reaction mixture was filtered at room temperature and then concentrated *in vacuo*. The resulting dark green solid was dissolved in *n*-pentane:dichloromethane (2:1) and filtered through alumina. Concentration *in vacuo* furnished another green solid. Sublimation (100 °C; 0.2 mm Hg^{-1}) furnished the title compound (*43*) as golden-yellow crystals (0.88 g, 68%), m.p. 158-160 °C [lit.[33] 158-161 °C]; $\upsilon_{max.}$ (*n*-hexane) 2 048 (CO), and 1 986 cm^{-1} (CO) [lit.[33] (CS_2) 2 045, and 1 980 cm^{-1}]; δ_H (220 MHz; $CDCl_3$) 2.41 (2H, d, *J* 8 Hz, Ph-C<u>H</u>=) 5.97 (2H, d, *J* 8 Hz, Ph-CH=C<u>H</u>-), and 7.33 (10H, 2 x -<u>Ph</u>); *m/z* (FAB) 346 (M^+, 22%), 318 (M^+-CO, 67%), 290 (M^+-2CO, 100%), and 262 (M^+-3CO, 58%).

(1,4-Diphenylbutadiene)tricarbonyliron(0) (*43*) [*via* a transfer reaction].-

(Cinnamaldehydeanil)tricarbonyliron(0) (*4*) (0.17 g, 0.50 mmol) and 1,4-diphenylbutadiene (*41*) (0.10 g, 0.50 mmol) were suspended in toluene (10 ml) and stirred at reflux under a nitrogen atmosphere for 48 hours. The light brown reaction mixture was allowed to cool, filtered through alumina, and then concentrated *in vacuo* to leave a light brown solid. This solid was sublimed *in vacuo* to leave the title complex (*43*) as yellow plates (0.04 g, 21%), m.p. 159-161 °C [lit.[33] 158-161 °C]; $\upsilon_{max.}$ (*n*-hexane) 2 045 (CO), and 1 985 cm^{-1}(CO) [lit.[33] (CS_2) 2 045, and 1 980 cm^{-1}]; δ_H (220 MHz; $CDCl_3$) 2.40 (2H, d, *J* 8 Hz, Ph-C<u>H</u>=), 5.94 (2H, d, *J* 8 Hz, Ph-CH=C<u>H</u>-), and 7.33 (10H, 2 x -<u>Ph</u>); *m/z* (FAB) 346 (M^+, 25%), 318 (M-CO, 58%), 290 (M-2CO, 100%), and 262 (M-3CO, 39%).

_N_-4-Chlorocinnamaldehydeanil (*46*).-

Cinnamaldehyde (*25*) (4.00 g, 30.3 mmol) was stirred in diethyl ether (25 ml) in an ice-water cooling bath. 4-Chloroaniline (3.86 g, 30.3 mmol) was added in one portion and the reaction mixture stirred for 6 hours. Dichloromethane (20 ml) was added to dissolve the resulting yellow suspension. The yellow solution was dried over magnesium sulphate, filtered, and concentrated *in vacuo* to leave a yellow solid. This solid was recrystallised from ethanol to leave the title compound (*46*) as pale yellow crystals (5.78 g, 79%), m.p. 106-108 °C [lit.[36] 108 °C]; $\upsilon_{max.}$ (cyclohexane) 1 620 (C=N), and 1 608 cm^{-1} (C=C) [lit.[34] (KBr disc) 1 625 cm^{-1}]; δ_H (220 MHz; $CDCl_3$) 7.15-7.63 (11H, broad m, Ph-CH=CH- and =N-C_6H_4Cl), and 8.30 (1H, d, *J* 7 Hz, -CH=N-) [lit.[35] 8.30 (1H)].

_N_-4-Methoxycinnamaldehydeanil (*44*).-

Cinnamaldehyde (*25*) (0.77 g, 5.8 mmol) was stirred in diethyl ether (20 ml) in an ice-water cooling bath. 4-Methoxyaniline (0.71 g, 5.8 mmol) was added and the reaction mixture stirred for 18 hours. The resulting yellow solution was diluted with diethyl ether (20 ml), dried over magnesium sulphate, filtered, and then concentrated *in vacuo* to leave a yellow solid. Recrystallisation of this solid from ethanol allowed the isolation of title compound (*44*) as pale yellow needles (1.19 g, 86%), m.p. 120-121 °C [lit.[36] 120 °C]; $\upsilon_{max.}$ (cyclohexane) 1 630 (C=N) and 1 615 cm^{-1} (C=C) [lit.[34] (KBr disc) 1 628 cm^{-1}]; δ_H (220 MHz; $CDCl_3$) 3.87 (3H, s, -OCH_3), 6.95 and 7.17 (2 x 2H, d, *J* 9 Hz, MeO-C_6H_4-), 7.25-7.65 (7H, m, Ph-CH=CH-), and 8.35 (1H, m, -N=CH-) [lit.[35] 8.28 (1H)].

1-(α-Isopropylethyl)-4-phenyl-1-azabuta-1,3-diene (*48*).-

Cinnamaldehyde (*25*) (2.64 g, 20.0 mmol) was stirred in diethyl ether (5 ml) in an ice-water cooling bath. 2-Amino-3-methylbutane (1.74 g, 20.0 mmol) was added dropwise over 5 minutes. The reaction was stirred for 0.25 hours, and then diluted with diethyl ether (10 ml). The resulting orange liquid was dried over magnesium sulphate, filtered and then concentrated *in vacuo* to provide the title compound (*48*) as a thermally unstable orange liquid (3.67 g, 98%), $\upsilon_{max.}$ (neat) 1 630 (C=N) and 1 615 cm^{-1} (C=C) [lit.[37] (neat) 1 640 and 1 620 cm^{-1}]; δ_H (220 MHz; $CDCl_3$) 0.88 (3H, d, *J* 7 Hz, CH_3-CH-C$\underline{H}_3$), 0.94 (3H, d, *J* 7 Hz, C$\underline{H}_3$-CH-CH_3), 1.20 (3H, d, *J* 7 Hz, N-CH(^{i}Pr)-C$\underline{H}_3$), 1.78 (1H, m, CH_3-C$\underline{H}$-CH_3), 2.90 (1H, m, -C$\underline{H}$(Me)(^{i}Pr)), 6.95 (2H, m, Ph-C$\underline{H}$=C$\underline{H}$-), 7.35-7.55 (5H, m, -$\underline{Ph}$) and 8.03 (1H, d, *J* 7 Hz, -N=C$\underline{H}$-) [lit.[37] (220 MHz; $CDCl_3$) 0.85 (3H, d, *J* 7 Hz), 0.95 (3H, d, *J* 7 Hz), 1.20 (3H, d, *J* 7 Hz), 1.75 (1H, m), 2.90 (1H, m), 7.00 (2H, m), 7.30 - 7.40 (5H, m), and 8.05 (1H, d, *J* 7 Hz)]; *m/z* (E.I.) 201 (M^+, 22%), and 158 (M-^{i}Pr, 100%) [lit.[37] 201 (11%) and 158 (100%)].

1-(α-*t*-Butylethyl)-4-phenyl-1-azabuta-1,3-diene (*49*).-

Cinnamaldehyde (*25*) (2.64 g, 20.0 mmol) was stirred in diethyl ether (5 ml) in an ice-water cooling bath. 2-Amino-3,3-dimethylbutane (2.02 g, 20.0 mmol) was added dropwise over 5 minutes. The reaction was stirred for 0.25 hours, and then diluted with diethyl ether (10 ml). The resulting pale yellow solution was dried over magnesium sulphate, filtered and then concentrated *in vacuo* to leave the title compound (*49*) as yellow crystals (3.33 g, 83%), m.p. 94.5-96.5 °C [lit.[37] 94.8-96.7 °C]; $\upsilon_{max.}$ (nujol) 1 636 (C=N) and 1 619 cm^{-1} (C=C) [lit.[37] (nujol) 1 635 and 1 620 cm^{-1}]; δ_H (220 MHz; $CDCl_3$) 0.93 (9H, s, -C(C$\underline{H}_3$)$_3$), 1.16 (3H, d, *J* 6 Hz, -CH-C$\underline{H}_3$), 2.87 (1H, q, *J* 6 Hz, -C$\underline{H}$(Me)(^{t}Bu)), 6.95 (2H, m, Ph-C$\underline{H}$=C$\underline{H}$-), 7.35-7.55 (5H, m, -$\underline{Ph}$), and 8.03 (1H, d, *J* 6 Hz, N=C$\underline{H}$-) [lit.[37] (220 MHz; $CDCl_3$) 0.90 (9H, s), 1.15 (3H, d, *J* 6 Hz), 2.90 (1H, q, *J* 6

Hz), 6.95 (2H, m), 7.30-7.55 (5H, m), and 8.05 (1H, d, *J* 6 Hz)]; *m/z* (E.I.) 215 (M^+, 15%), and 158 (M-^{t}Bu, 100%) [lit.[37] 215 (6%), and 158 (100%)].

(*N*-4-Methoxycinnamaldehydeanil)tricarbonyliron(0) (*45*).-

(Cinnamaldehyde)tricarbonyliron(0) (*42*) (0.13 g, 0.49 mmol) and *N*-4-methoxycinnamaldehydeanil (*44*) (0.12 g, 0.49 mmol) were suspended in toluene (10 ml) and stirred at 85 °C under a nitrogen atmosphere for 14.5 hours. The brown reaction mixture was allowed to cool, filtered through alumina, and then concentrated *in vacuo* to leave a dark red solid. This solid was chromatographed on silica using 40-60 petroleum either:diethyl ether (15:1). The red-orange band was collected and concentrated *in vacuo* to leave the title complex (*45*) as dark red crystals (0.14 g, 75%), $\upsilon_{max.}$ (cyclohexane) 2 057 (CO), 1 997 (CO), and 1 985 cm^{-1} (CO) [lit.[6] (cyclohexane) 2 056, 1 997 and 1 984 cm^{-1}]; δ_H (220 MHz; $CDCl_3$) 3.43 (1H, d, *J* 9 Hz, Ph-C<u>H</u>=), 3.80 (3H, s, -OC<u>H</u>$_3$), 5.74 (1H, dd, *J* 3 and 9Hz; Ph-CH=C<u>H</u>-), 6.80 and 6.95 (2 x 2H, d, *J* 9 Hz, -C_6<u>H</u>$_4$OMe), 6.95 (2H, d, *J* 9 Hz, -<u>Ph</u>), and 7.25-7.40 (6H, broad m, -N=C<u>H</u>- and <u>Ph</u>-) [lit.[6] (100 MHz; CS_2) 3.26 (1H), 3.65 (3H), and 5.55 (1H)]; *m/z* (FAB) 378 (M+1, 11%), 349 (M-CO, 19%), 321 (M-2CO, 17%), 293 (M-3CO, 100%), and 237 (M-Fe(C0)$_3$, 15%).

(*N*-4-Chlorocinnamaldehydeanil)tricarbonyliron(0) (*47*).-

(Cinnamaldehyde)tricarbonyliron(0) (*42*) (0.14 g, 0.5 mmol) and *N*-4-chlorocinnamaldehydeanil (*46*) (0.12, 0.5 mmol) were suspended in toluene (10 ml) and stirred at 85 °C under a nitrogen atmosphere for 14.5 hours. The brown reaction mixture was allowed to cool, filtered through alumina, and the concentrated *in vacuo* to leave a dark red solid. This solid was chromatographed on silica using 40-60 petroleum ether:diethyl ether (15:1). The orange band was collected and concentrated *in vacuo* to

leave the title complex (*47*) as orange-red needles (0.09 g, 46%), $\upsilon_{max.}$ (cyclohexane) 2 060 (CO), 2 001 (CO), and 1 989 cm^{-1} (CO) [lit.[6] (cyclohexane) 2 060, 2 001, and 1 989 cm^{-1}]; δ_H (220 MHz; $CDCl_3$) 3.41 (1H, d, *J* 9 Hz, Ph-C<u>H</u>=), 5.77 (1H, dd, *J* 9 and 4 Hz, Ph-CH=C<u>H</u>-), 6.89 and 7.19 (2 x 2H, d, *J* 9 Hz, -$C_6\underline{H}_4Cl$), 7.19 (2H, d, *J* 9 Hz, -<u>Ph</u>), and 7.28-7.42 (6H, broad m, <u>Ph</u>- and -N=C<u>H</u>-) [lit.[6] (CS_2) 3.25 (1H), and 5.64 (1H)]; *m/z* (FAB) 382 (M+1, 15%), 353 (M-CO, 7%), 325 (M-2CO, 11%), 297 (H-3CO, 100%), and 241 (M-$Fe(CO)_3$, 42%).

[1-(1-iso-Propylethyl)-4-phenyl-1-azabuta-1,3-diene]tri- carbonyliron(0) (*50*).-

(Cinnamaldehyde)tricarbonyliron(0) (*42*) (0.14 g, 0.51 mmol) and 1-(α-isopropylethyl)-4-phenyl-1-azabuta-1,3-diene (*48*) were suspended in toluene (10 ml) and stirred at reflux under a nitrogen atmosphere for 7.5 hours. The brown reaction mixture was allowed to cool, filtered through alumina, and then concentrated *in vacuo* to leave a dark brown solid. This solid was chromatographed on silica using 40-60 petroleum ether:diethyl ether (15:1) as eluent. The orange-yellow band was collected and concentrated *in vacuo* to leave the title complex (*50*) as a thermally unstable orange solid (0.08 g, 46%), a 1:1 mixture of diastereoisomers, $\nu_{max.}$ (hexane) 2 054 (CO), 1 993 (CO), and 1 976 cm^{-1} (CO) [lit.[37] (hexane) 2 050, 1 995, and 1 975 cm^{-1}]; δ_H (400 MHz, $CDCl_3$) 0.81-1.10 (9H, m, 3 x -$C\underline{H}_3$), 1.61-1.71 (1H, broad m, -$C\underline{H}(CH_3)_2$), 1.73-1.82 (1H, m, -C<u>H</u>(Me)(^{i}Pr)), 2.95 and 3.00 (1H, d, *J* 9 Hz, Ph-C<u>H</u>=), 5.43 and 5.50 (1H, dd, *J* 3 and 9 Hz, Ph-CH=C<u>H</u>-), 6.52 and 6.61 (1H, d, *J* 3 Hz, -N=C<u>H</u>-), and 7.15-7.28 (5H, broad m, -<u>Ph</u>) [lit.[37] (220 MHz; $CDCl_3$) 0.8-1.0 (9H, m), 1.6-1.7 (1H, m), 1.75-1.85 (1H, m), 2.95 and 3.0 (1H, d, *J* 9 Hz), 5.45 and 5.50 (1H, dd, J 3 and 9 Hz), 6.55 and 6.65 (1H, d, *J* 3 Hz), and 7.15-7.30 (5H, m)]; *m/z* (FAB) 342 (M+1, 100%), 313 (M-CO, 19%), 285 (M-2CO, 48%), 257 (M-3CO, 52%) and 202 (MH-$Fe(CO)_3$, 62%) [lit.[37] (FAB) 342 (100%), 314 (20%), 286 (24%), 258 (19%), and 202 (78%)].

[1-(α-*t*-Butylethyl)-4-phenyl-1-azabuta-1,3-diene]tri-carbonyliron(0) (*51*).-

(Cinnamaldehyde)tricarbonyliron(0) (*42*) (0.14 g, 0.5 mmol) and 1-(α-*t*-butylethyl)-4-phenyl-1-azabuta-1,3-diene (*49*) (0.11 g, 0.5 mmol) were suspended in toluene (10 ml) and stirred at reflux under a nitrogen atmosphere for 7.5 hours. The brown reaction mixture was allowed to cool, filtered through alumina, and then concentrated *in vacuo* to leave a dark red-brown liquid. This liquid was chromatographed on silica using 40-60 petroleum ether:diethyl ether (15:1) as eluent. The orange band was collected and concentrated *in vacuo* to leave the title complex (*51*) as orange needles (0.04 g, 25%), a 95:5 mixture of diastereoisomers; $\upsilon_{max.}$ (hexane) 2 052 (CO), 1 998 (CO), and 1 977 cm^{-1} (CO) [lit.[36] (hexane) 2 050, 1 995 and 1 975 cm^{-1}]; δ_H (400 MHz; $CDCl_3$) major diastereoisomer: 0.85 (9H, s, -C(C<u>H</u>$_3$)$_3$), 1.05 (3H, d, *J* 6 Hz, -CH(C<u>H</u>$_3$)), 1.69 (1H, q, *J* 6 Hz, -C<u>H</u>(Me)(^{t}Bu)), 3.00 (1H, d, *J* 9 Hz, Ph-C<u>H</u>-), 5.37 (1H, dd, *J* 4 and 6 Hz, Ph-CH=C<u>H</u>-), 6.50 (1H, d, *J* 4 Hz, -N=C<u>H</u>-), and 7.12-7.25 (5H, broad m, -<u>Ph</u>) [lit.[37] (400 MHz; $CDCl_3$) 0.85 (9H, s), 1.04 (3H, d, *J* 6 Hz), 1.63 (1H, q, *J* 6 Hz), 3.00 (1H, d, *J* 9 Hz), 5.36 (1H, dd, *J* 4 and 9 Hz), 6.50 (1H, d, *J* 4 Hz), and 7.10-7.25 (5H, m)]; minor diastereoisomer: 0.90 (9H, s, -C(C<u>H</u>$_3$)$_3$), 0.96 (3H, d, *J* 6 Hz, -CHC<u>H</u>$_3$), 2.18 (1H, q, *J* 6 Hz, -C<u>H</u>(Me)(^{t}Bu)), 2.95 (1H, d, *J* 9 Hz, Ph-C<u>H</u>=) 5.41 (1H, dd, *J* 4 and 9 Hz), 6.81 (1H, d, *J* 4 Hz, -N=C<u>H</u>-), and 7.12-7.25 (5H, broad m, <u>Ph</u>-) [lit.[37] (400M $CDCl_3$) 0.89 (9H, s), 0.95 (3H, d, *J* 6 Hz), 2.19 (1H, q, *J* 6 Hz), 2.95 (1H, d, *J* 9 Hz), 5.41 (1H, dd, *J* 4 and 9 Hz), 6.81 (1H, d, *J* 4 Hz, -N=C<u>H</u>-), and 7.10-7.25 (5H, broad m)]; *m/z* (FAB) 356 (M+1, 100%), 327 (M-CO, 21%), 299 (M-2CO, 36%)) 270 (M-3CO, 56%), and 215 (MH-Fe(CO)$_3$, 67%) [lit.[37] (FAB) 356 (100%), 328 (MH-CO, 18%), 300 (MH-2CO, 26%), 271 (M-3CO, 33%) and 216 (70%)].

(Methyl sorbate)tricarbonyliron(0) (*28*).-

(*N*-4-Chlorocinnamaldehydeanil)tricarbonyliron(0) (*47*) (0.22 g, 0.57 mmol) and methyl sorbate (*27*) (0.07 g, 0.57 mmol) were suspended in toluene (10 ml) and stirred at reflux under a nitrogen atmosphere for 72 hours. The brown reaction mixture was allowed to cool, filtered through alumina, and concentrated *in vacuo* to leave a light brown liquid. This liquid was chromatographed on silica using 40-60 petroleum ether:diethyl ether (19:1). The yellow band was collected and concentrated *in vacuo* to leave the title complex (*28*) as yellow crystals (0.03 g, 35%), $\nu_{max.}$ ($CHCl_3$) 2 090 (CO), 2 055 (CO), and 1 750 cm^{-1} (C=O) [lit.[26] ($CHCl_3$) 2 100, 2 050, and 1 725 cm^{-1}]; δ_H (220 MHz; $CDCl_3$) 1.00 (1H, d, *J* 8 Hz, $MeCO_2C\underline{H}$=), 1.37 (3H, s, $C\underline{H}_3CO_2$-), 1.48 (3H, s, $C\underline{H}_3CH$=), 1.65 (1H, d, *J* 8 Hz, CH_3-C$\underline{H}$=), 5.27 (1H, dd, *J* 6 and 8 Hz, CH_3CH=C$\underline{H}$-), and 5.83 (1H, dd, *J* 6 and 8 Hz, $MeCO_2CH$=C$\underline{H}$=) [lit.[38] (220 MHz; $CDCl_3$) 1.0 (1H, d, *J* 9 Hz), 1.45 (2H, m), 3.65 (3H, s), 5.25 (1H, m), and 5.80 (1H, dd, *J* 7 and 9 Hz); *m/z* (FAB) 267 (MH, 34%), 239 (MH-CO, 62%), 211 (MH-2CO, 28%), and 183 (MH-3CO, 100%) [lit.[38] 266 (9%), 238 (32%), 210 (59%), and 182 (51%)].

Attempted Diels-Alder reactions with cinnamaldehydeanil (*5*) and (cinnamaldehydeanil)tricarbonyliron(0) (*4*).-

a. Maleic anhydride (0.03 g, 0.29 mmol) (*52*) and (cinnamaldehydeanil)tricarbonyliron(0) (*4*) (0.07 g, 0.25 mmol) were dissolved in dichloromethane (5 ml) and stirred at 40 °C for 4.5 hours under a nitrogen atmosphere. The turbid, orange solution was concentrated *in vacuo*, dissolved in diethyl ether and filtered through alumina. Concentration *in vacuo* furnished fine orange needles. Recrystallisation from *n*-heptane allowed the isolation of starting material (*4*) as orange-red needles (0.06 g, 65%), $\upsilon_{max.}$ (nujol) 2 060 (CO), 1 985 (CO), and 1 955 cm^{-1} (CO); δ_H (220 MHz; $CDCl_3$) 3.40 (1H, d, *J* 9 Hz, Ph-C$\underline{H}$=),

5.75 (1H, dd, *J* 9 and 2 Hz, Ph-CH=C<u>H</u>-), and 6.95-7.50 (11H, broad m, 2 x <u>Ph</u>- and N=C<u>H</u>-); *m/z* (FAB) 347 (M^+, 29%), 319(M^+-CO, 58%), 291 (M^+-2CO, 100%), and 263 (M^+-3CO, 43%).

b. <u>Using trimethyloxamine (*86*)</u>

(Cinnamaldehydeanil)tricarbonyliron(0) (*4*) (0.05 g, 0.15 mmol), dimethyl fumarate (0.04 g, 0.26 mmol) and trimethyloxamine (*86*) (0.06 g, 0.55 mmol) were dissolved in acetone (5 ml) to give an orange solution and stirred at room temperature for 5 hours under a nitrogen atmosphere. The resulting turbid, orange solution was filtered, the residue washed with acetone and the combined organic phases concentrated *in vacuo* to leave a light brown solid. Recrystallisation of this solid from *n*-heptane allowed the isolation of starting complex (*4*) (0.04 g, 75%), $\upsilon_{max.}$ (nujol) 2 058 (CO), 1 984 (CO), and 1 955 cm^{-1} (CO); δ_H (220 MHz; $CDCl_3$) 3.41 (1H, d, *J* 9 Hz, Ph-C<u>H</u>=), 5.78 (1H, dd, *J* 9 and 2 Hz, Ph-CH=C<u>H</u>-), and 6.90 -7.56 (11H, broad m, 2 x <u>Ph</u>- and -N=C<u>H</u>-); *m/z* (FAB) 347 (M^+, 32%), 319 (M^+-3CO, 62%), 291 (M^+-2CO, 100%), and 263 (M^+-3CO, 41%).

c. <u>Using phenyltriazadinedione (*82*) at low temperature</u>

(Cinnamaldehydeanil)tricarbonyliron(0) (*4*) (0.08 g, 0.23 mmol) and phenyltriazolinedione (*82*) (0.04 g, 0.23 mmol) were dissolved in acetone (5 ml). The resulting dark red solution was stirred at -50 °C under a nitrogen atmosphere for 5 hours and then filtered. The residue was washed with acetone (2 x 1 ml). The combined filtrates were concentrated *in vacuo* to leave a dark brown solid. This solid was dissolved in diethyl ether (10 ml) and filtered through alumina. The orange filtrate was concentrated *in vacuo* to leave cinnamaldehydeanil (*5*) as yellow crystals (0.05 g, 94%), m.p. 107-109 °C; $\upsilon_{max.}$ (nujol) 1 622 (C=N) and 1 571 cm^{-1} (C=C); δ_H (220 MHz; $CDCl_3$) 8.31 (1H, m, Ph-N=C<u>H</u>-), and 7.20-7.60 (12H, m, 2 x <u>Ph</u>- and Ph-C<u>H</u>-C<u>H</u>).

1-Phenyl-2-styryl-1,2-dihydropyridinetetracarboxylic acid-(3,4,5,6)-tetramethyl ester (*93*).-

(Cinnamaldehydeanil)tricarbonyliron(0) (*4*) (0.14 g, 0.4 mmol) was cooled to -15 °C under a carbon monoxide atmosphere. Dimethyl acetylenedicarboxylate (0.66 g, 4.6 mmol) dissolved in THF (10 ml) was added portionwise over 0.5 hours, maintaining the temperature at about -15 °C. The orange-red solution was stirred at -15 °C for 7 hours. The reaction mixture was allowed to warm to room temperature over 2 hours and then stirred for an additional 11 hours. The dark red reaction mixture was then concentrated *in vacuo* to furnish a dark red gum. Chromatography on silica with acetone:60-80 petroleum ether (2:3) as eluent yielded a yellow solid. Recrystallisation from methanol gave the title compound (*93*) as yellow plates (0.07 g, 51%), m.p. 161-163 °C [lit.[57] 161-165 °C]; $\upsilon_{max.}$ ($CHCl_3$) 1 750 (C=O), 1 730 (C=O), 1 710 (C=O), 745 (Ar C-H), and 710 cm^{-1} (Ar C-H) [lit.[57] (KBr) 1 740, 1 708, 1 688, 738 and 693 cm^{-1}]; δ_H (220 MHz; $CDCl_3$) 3.55 (3H, s, $-CO_2C\underline{H}_3$), 3.65 (3H, s, $-CO_2C\underline{H}_3$), 3.70 (3H, s, $-CO_2C\underline{H}_3$) 3.90 (3H, s, $-CO_2C\underline{H}_3$), 5.45 (1H, d, *J* 6 Hz, Ph-C<u>H</u>=), 6.30 (1H, dd, *J* 6 and 18 Hz, Ph-CH=C<u>H</u>-), 6.70 (1H, d, *J* 18 Hz, N-C<u>H</u>-), and 7.35 (10H, m, 2 x <u>Ph</u>-) [lit.[57] ($CDCl_3$) 3.60 (3H, s), 3.70 (3H, s), 3.75 (3H, s), 3.90 (3H, s), 5.50 (1H, d), 6.41 (1H, d), 6.70 (1H, s) and 7.40 (10H, m)]; *m/z* (E.I.) 492 (M^+, 23%), and 433 (M^+-CO_2Me, 100%).

***N*-(Benzylidene)-2-propen-1-amine (*109*).-**

Allylamine (20 ml, 15.20 g, 0.27 mmol) was cooled to 2 °C with stirring. Benzaldehyde (27 ml, 28.19 g, 0.27 mmol) was added dropwise over 0.25 hours, maintaining the temperature at 3 °C after an initial exotherm to 15 °C. The resulting clear, pale yellow solution was allowed to warm to room temperature and stirred for 1.25 hours. Sodium hydroxide (3 pellets) was added to the milky reaction mixture and the organic layer

separated before being dried over sodium carbonate to give a clear, pale yellow liquid. This liquid was distilled *in vacuo* to furnish the title compound (*109*) as a clear, colourless liquid (30.57 g, 79%), b.p. 61-69 °C; 0.2 mm Hg; $\upsilon_{max.}$ (neat) 1 652 (C=N) and 1 575 cm^{-1} (C=C) [lit.[62] (neat) 1 650 cm^{-1}]; δ_H (220 MHz; CCl_4) 4.20 (2H, d, *J* 9 Hz, =N-C<u>H</u>$_2$-), 5.07 (1H, dd, J_{gem} 2 Hz, J_{cis} 12 Hz) and 5.14 (1H, dd, J_{gem} 2 Hz, J_{trans} 19 Hz) (-CH=C<u>H</u>$_2$), 6.10 (1H, m, -C<u>H</u>=CH$_2$), 7.40 (3H, m, <u>Ar</u>-), 7.65 (2H, m, <u>Ar</u>-), and 8.25 (1H, s, -N=C<u>H</u>-Ph) [lit.[63] (CCl_4) 4.25 (2H, m), 5.15 (2H, m), 6.17 (1H, m), 7.20 and 7.40 (5H, m), and 8.22 (1H, t)].

N-(4-Methoxybenzylidene)-2-propen-1-amine (*110*).-

4-Methoxybenzaldehyde (1.46 g, 10.7 mmol) was mixed with ethanol (5 ml) and stirred in an ice-water cooling bath. Allylamine (0.63 g, 11.0 mmol) was added portionwise over 10 minutes. The resulting solution was stirred in the ice bath for 0.5 hours and then at room temperature for 4 hours. The clear, pale yellow reaction mixture was diluted with ethanol (5 ml), dried over sodium carbonate, filtered, and concentrated *in vacuo*. This yellow liquid was distilled *in vacuo* to furnish the title compound (*110*) as a clear, colourless liquid (1.85 g, 98%), b.p. 112 °C; 0.2 mm Hg; $C_{11}H_{13}NO$ requires 175.0994, found (M^+) 175.0993; $\upsilon_{max.}$ (neat) 1 650 (C=N), 1 605 (C=C), and 1 250 cm^{-1} (Me-O-C); δ_H (220 MHz, $CDCl_3$) 3.82 (3H, s, -OC<u>H</u>$_3$), 4.25 (2H, d, *J* 6 Hz, =N-C<u>H</u>$_2$-), 5.18 (1H, dd, J_{gem} 2 Hz, J_{cis} 12 Hz) and 5.25 (1H, dd, J_{gem} 2 Hz, J_{trans} 19 Hz) (-CH=C<u>H</u>$_2$), 6.13 (1H, m, -C<u>H</u>=CH$_2$), 6.98 and 7.77 (2 x 2H, d, *J* 9 Hz, -C$_6$<u>H</u>$_4$OMe), and 8.28 (1H, s, -N=C<u>H</u>-) [lit.[64] (CCl_4) 3.44 (3H), 3.97 (2H), 4.97 (2H), 5.90 (1H), 7.00 (4H), and 7.83 (1H)]; *m/z* (E.I.) 175 (M^+, 55%), 174 (M^+-1,100%) [lit.[65] 175 (69%), and 174 (100%)].

***N*-(4-Chlorobenzylidene)-2-propen-1-amine (*111*).-**

4-Chlorobenzaldehyde (1.32 g, 9.4 mmol) was dissolved in ethanol (10 ml) and stirred in an ice-water cooling bath. Allylamine (0.56 g, 9.8 mmol) was added portionwise over 0.25 hours. The reaction mixture was stirred in the ice bath for 0.5 hours and then at room temperature for 2 hours. The resulting pale yellow solution was diluted with ethanol (10 ml), dried over sodium carbonate, filtered, and then concentrated *in vacuo* to leave a pale yellow gum. This gum was distilled *in vacuo* to furnish the title compound (*111*) as a clear, colourless liquid (1.62 g, 96%), b.p. 87 °C; 0.2 mm Hg^{-1}; $C_{10}H_{10}NCl$ requires 179.0499, found (M^+) 179.0493; $\upsilon_{max.}$ ($CHCl_3$) 1 655 (C=N), and 1 600 cm^{-1} (C=C); δ_H (220 MHz; $CDCl_3$) 4.28 (2H, d, *J* 6 Hz, =N-C<u>H</u>$_2$-), 5.25 (1H, dd, J_{gem} 2 Hz, J_{cis} 12 Hz) and 5.29 (1H, dd, J_{gem} 2 Hz, J_{trans} 19 Hz) (-CH=C<u>H</u>$_2$), 6.15 (1H, m, -C<u>H</u>=CH$_2$), 7.47 and 7.78 (2 x 2H, d, *J* 9 Hz, -C$_6$<u>H</u>$_4$Cl), and 8.31 (1H, s, -N=C<u>H</u>-); *m/z* (E.I.) 178 (M^+- 1, 100%).

***N*-(4-Cyanobenzylidene)-2-propen-1-amine (*112*).-**

4-Cyanobenzaldehyde (1.06 g, 8.1 mmol) was suspended in ethanol (10 ml) and stirred in an ice-water cooling bath. Allylamine (0.48 g, 8.4 mmol) was added dropwise over 2 minutes. The pale yellow reaction mixture was stirred in the ice bath for 0.5 hours and then at room temperature for 3.75 hours. The resulting yellow solution was diluted with ethanol (10 ml), dried over sodium carbonate, filtered, and concentrated *in vacuo* to leave a yellow liquid. This liquid was distilled *in vacuo* to furnish the title compound (*112*) as a clear colourless liquid (1.18 g, 86%), b.p. 82 °C; 0.2 mm Hg; $C_{11}H_{10}N_2$ requires 170.0842, found (M^+) 170.0847; $\upsilon_{max.}$ (neat) 2 260 (C≡N), and 1 650 (C=N); δ_H (220 MHz; $CDCl_3$) 4.35 (2H, d, *J* 5 Hz, =N-C<u>H</u>$_2$-), 5.25 (1H, dd, J_{gem} 2 Hz, J_{cis} 12 Hz) and 5,28 (1H, dd, J_{gem} 2 Hz, J_{trans} 19 Hz) (-CH=C<u>H</u>$_2$), 6.13 (1H, m, -C<u>H</u>=CH$_2$), 7.78 and 7.92 (2 x2H, d, *J* 9 Hz, -C$_6$<u>H</u>$_4$CN), and 8.41 (1H, s, -N=C<u>H</u>-); *m/z* (E.I.) 170 (M^+, 43%), and 169 (M^+-1, 100%).

_N_-(4-Nitrobenzylidene)-2-propen-1-amine (*113*).-

4-Nitrobenzaldehyde (0.58 g, 3.8 mmol) was dissolved in ethanol (18 ml) and added to allylamine (0.24 g, 4.2 mmol) at 2 °C with stirring. The pale yellow solution was allowed to warm to room temperature and stirred for 2.75 hours. Concentration *in vacuo* furnished "fluffy" yellow needles. These needles were dissolved in carbon tetrachloride (5 ml), filtered, and concentrated *in vacuo* to furnish the title compound (*113*) as orange crystals (0.72 g, 99%), m.p. 43-44 °C; found: C, 62.89; H, 5.29; N, 14.51. $C_{10}H_{10}N_2O_4$ requires C, 63.15; H, 5.30; N, 14.73 %; $\upsilon_{max.}$ (CCl_4) 1 530 (ArN=O), and 1 350 cm^{-1} (ArN=O); δ_H (400 MHz; $CDCl_3$) 4.35 (2H, dd, *J* 1.5 and 6 Hz, =N-C<u>H</u>$_2$-), 5.23 (1H, dd, J_{gem} 1.5 Hz, J_{cis} 17 Hz) and 5.26 (1H, dd, J_{gem} 1.5 Hz, J_{trans} 24 Hz) (-CH=C<u>H</u>$_2$), 6.10 (1H, ddt, *J* 6, 17, and 24 Hz, -C<u>H</u>=CH$_2$), 7.95 and 8.29 (2 x 2H, d, *J* 9 Hz, -C$_6$<u>H</u>$_4$NO$_2$), and 8.39 (1H, s, -C<u>H</u>=N-); *m/z* (E.I.) 190 (M^+, 15%), and 41 (M-$C_7H_5N_2O_2$, 100%) [lit.[65] 190 (36%), and 41 (100%)].

_N_-(Benzylidene)-1-propen-1-amine (*114*).-

N-(Benzylidene)-2-propen-1-amine (*109*) (3.31 g, 22.8 mmol) was dissolved in DMSO (15 ml) and potassium *t*-butoxide (0.28 g, 2.28 mmol) added portionwise over 5 minutes. The dark brown reaction mixture was stirred at 25 °C for 1 hour and then poured into water (distilled, 15 ml). This aqueous solution was extracted with ethyl acetate (4 x 20 ml), and the combined organic phases washed with water (distilled, 3 x 15 ml), dried over sodium carbonate, filtered, and concentration *in vacuo* to leave a light brown oil. This oil was distilled *in vacuo* to give the title compound (*114*) as a light brown oil (2.95 g, 89%), a 1:2 mixture of Z_{cc}- and E_{cc}- isomers, b.p. 60-65 °C; 0.2 mm Hg; $\upsilon_{max.}$ (neat) E_{cc}-isomer: 1 660 (C=N), and 1 610 cm^{-1} (C=C); Z_{cc}-isomer: 1 645 (C=N) and 1 570 cm^{-1} (C=C) [lit.[63]

(neat) 1 660, 1 645, 1 610, 1 575 and 1 570 cm^{-1}]; δ_H (220 MHz; CCl_4) E_{cc}-isomer: 1.90 (*3*H, d, *J* 7 Hz, -C<u>H</u>$_3$), 6.10 (1H, dq, *J* 13 and 7 Hz, =C<u>H</u>-CH_3), 6.75 (1H, m, N-C<u>H</u>=CH-CH_3), 7.35 and 7.75 (5H, m, -<u>Ph</u>), and 8.05 (1H, s, Ph-C<u>H</u>=N-); Z_{cc}-isomer: 2.05 (3H, d, *J* 7 Hz, -C<u>H</u>$_3$), 5.45 (1H, dq, *J* 10 and 7 Hz, =C<u>H</u>-CH_3), 6.75 (1H, m, N-C<u>H</u>=CH-CH_3), 7.35 and 7.75 (5H, m, -<u>Ph</u>), and 8.10 (1H, s, Ph-C<u>H</u>=N-) [lit.[63] (60 MHz; CCl_4) E_{cc}-isomer: 1.85 (3H, d, *J* 7.5 Hz), 6.15 (1H, m), 6.85 (1H, m), 7.50 and 7.80 (5H, m), and 8.10(1H, s); Z_{cc}-isomer: 2.05 (3H, d, *J* 7.5 Hz), 5.50 (1H, m), 6.80 (1H, m), 7.50 and 7.80 (5H, m), and 8.20 (1H, s)]; *m/z* (E.I.) 145 (M^+, 100%) [lit.[65] 145 (100%)].

_N_-(4-Methoxybenzylidene)-1-propen-1-amine (*115*).-

_N_-(4-Methoxybenzylidene)-2-propen-1-amine (*110*) (2.33g, 1.33 mmol) was diluted with THF (20 ml) and stirred in an ice-water cooling bath. Potassium *t*-butoxide (1.62 g, 1.33 mmol) was suspended in THF (20 ml) and added to the imine solution to give an orange solution. The reaction mixture was stirred for 0.75 hours until the orange solution became brown, and then quenched with water (distilled, 20 ml). Extraction with ethyl acetate (2 x 15 ml), washing the organic layer with water (distilled, 10 ml), drying over sodium carbonate and filtering allowed a light brown liquid to be isolated by concentration *in vacuo*. This brown liquid was distilled *in vacuo* to furnish the title compound (*115*) as a clear, colourless liquid (2.26 g, 92%), a 1.2:1 mixture of Z_{cc}- and E_{cc}-isomers, b.p. 83 °C; 0.2 mm Hg [lit.[67] 76-80 °C; 0.05 mm Hg]; $C_{11}H_{13}NO$ requires 175.0994, found (M^+) 175.0991; $\upsilon_{max.}$ ($CHCl_3$) 1 610 (C=N), 1 590 (C=C), and 1 250 cm^{-1} (Me-O-C); δ_H (220 MHz; $CDCl_3$) E_{cc}-isomer: 1.80 (3H, d, *J* 7 Hz, -C<u>H</u>$_3$), 3.81 (3H, s, -OC<u>H</u>$_3$), 6.10 (1H, dq, *J* 13 and 7 Hz, =C<u>H</u>-CH_3), 6.95 (1H, m, N-C<u>H</u>=CH-CH_3), 7.75 (4H, m, -<u>Ar</u>), and 8.05 (1H, s, Ph-C<u>H</u>=N-); Z_{cc}-isomer: 2.05 (3H, d, *J* 7Hz, -C<u>H</u>$_3$), 5.45 (1H, dq, *J* 10 and 7 Hz, =C<u>H</u>-CH_3), 6.90 (1H, m, N-C<u>H</u>=CH-CH_3), 7.75 (4H, m, -<u>Ar</u>), and 8.10 (1H, s, Ph-C<u>H</u>=N-) [lit.[67] (250 MH_3; $CDCl_3$) E_{cc}-isomer: 1.82 (3H, d, *J* 6.8 Hz), 3.83 (3H, s), 6.07 (1H, m),

6.79 (1H, d), and 8.09 (1H, s); Z_{cc}-isomer: 2.04 (3H, d, *J* 7 Hz), 3.84 (3H, s, -OC<u>H</u>$_3$), 5.44 (1H, m), 6.73 (1H, d), and 8.13 (1H, s). *n.b.* signals due to phenyl protons not given]; *m/z* (E.I.) 175 (M^+, 60%), and 174 (M^+-1, 100%).

_N_-(4-Chlorobenzylidene)-1-propen-1-amine (*116*).-

N-(4-Chlorobenzylidene)-2-propen-1-amine (*111*) (0.73 g, 4.04 mmol) was diluted with THF (10 ml) and stirred in an ice-water cooling bath. Potassium *t*-butoxide (0.14 g, 1.12 mmol) was suspended in THF (10 ml) and added to the imine solution in one portion. The imine solution immediately turned red. After stirring for 1 minute the red solution turned brown and the reaction was quenched with water (distilled, 20 ml). Extraction with ethyl acetate (2 x 10 ml), washing the organic layer with water (20 ml), drying over sodium carbonate, and filtration, allowed the isolation of an orange liquid by concentration *in vacuo*. This orange liquid was distilled *in vacuo* to furnish the title compound (*116*) as a clear, colourless liquid (0.70 g, 86%), a 1.7:1 mixture of E_{cc}- and Z_{cc}-isomers, b.p. 79 °C; 0.2 mm Hg; $C_{10}H_{10}NCl$ requires 179.0499, found (M^+) 179.0492; $\upsilon_{max.}$ ($CHCl_3$) 1 610 (C=N), and 1 590 cm^{-1} (C=C); δ_H (220 MHz; $CDCl_3$) E_{cc}-isomer: 1.86 (3H, d, *J* 7 Hz, -C<u>H</u>$_3$), 6.23 (1H, dq, *J* 13 and 7 Hz, =C<u>H</u>-CH$_3$), 6.85 (1H, m, N-C<u>H</u>=CH-CH$_3$), 7.45 and 7.78 (4H, m, -<u>Ar</u>), and 8.15 (1H, s, Ph-C<u>H</u>=N); Z_{cc}-isomer: 2.07 (3H, d, *J* 7 Hz, -C<u>H</u>$_3$), 5.58 (1H, dq, *J* 10 and 7 Hz, =C<u>H</u>-CH$_3$), 6.85 (1H, m, N-C<u>H</u>=CH-CH$_3$), 7.45 and 7.78 (4H, m, -<u>Ar</u>), and 8.20 (1H, s, Ph-C<u>H</u>=N); *m/z* (E.I.) 179 (M^+-1, 100%).

Attempted synthesis of [*N*-(Benzylidene)-1-propen-1-amine]- tricarbonyliron(0) (*117*).-

a. <u>With di-iron enneacarbonyl (*17*)</u>

N-(Benzylidene)-1-propen-1-amine (*114*) (0.62 g, 4.3 mmol) and di-iron

enneacarbonyl (*17*) (1.56 g, 4.3 mmol) were suspended in toluene (10 ml) and heated to 40 °C for 2.5 hours under a nitrogen atmosphere. The resulting dark brown mixture was filtered and concentrated *in vacuo* to leave a brick red oil which was identified as the starting material (*114*) (0.61 g, 98%), δ_H (220 MHz; CCl_4) 1.85 and 2.05 (3H, d, *J* 8 Hz, -C<u>H</u>$_3$), 5.45 and 6.10 (1H, m, C=C<u>H</u>-), 6.75 (1H, m, NC<u>H</u>), 7.40 and 7.80 (5H, m, -Ph), and 8.10 and 8.15 (1H, s, N=C<u>H</u>).

b. <u>With iron pentacarbonyl (*26*)</u>

N-(Benzylidene)-1-propen-1-amine (*114*) (0.40 g, 2.8 mmol) and trimethyloxamine (*86*) (1.24 g, 11.2 mmol) were dissolved in benzene (15 ml) and cooled to -10 °C. Iron pentacarbonyl (*26*) (1.13 g, 5.8 mmol) was added and the resulting light brown solution stirred under a nitrogen atmosphere for 1.5 hours at 0 to -5 °C. The reaction mixture was filtered and the residue washed with benzene (2 x 5 ml). The combined organic phases were concentrated *in vacuo* to leave the starting material (*114*) as a brick red oil (0.31 g, 77%), δ_H (220 MHz; CCl_4) 1.90 and 2.10 (3H, d, *J* 8 Hz, -C<u>H</u>$_3$), 5.50 and 6.15 (1H, m, C=C<u>H</u>-), 6.75 (1H, m, NC<u>H</u>), 7.40 and 7.80 (5H, m, -Ph), and 8.10 and 8.15 (1H, s, N=C<u>H</u>-).

c. <u>Mild complexation</u>

N-(Benzylidene)-1-propen-1-amine (*114*) (0.35 g, 2.4 mmol) and di-iron enneacarbonyl (*17*) (0.89 g, 2.5 mmol) were suspended in diethyl ether (10 ml) and stirred at room temperature for 0.5 hours under a nitrogen atmosphere. The temperature was then increased to 30 °C and stirring continued for a further 2.5 hours. The light brown reaction mixture was filtered, and concentrated *in vacuo* to give an air-sensitive dark red oil (0.30 g), $\upsilon_{max.}$ ($CHCl_3$) 2 010 (Fe-C≡O), and 1 975 cm^{-1} (Fe-C≡O).

$Fe_2(CO)_6$ complex (*118*).-

N-(4-Methoxybenzylidene)-1-propen-1-amine (1.00 g, 5.7 mmol) (*115*) and di-iron enneacarbonyl (*17*) (2.11 g, 5.8 mmol) were suspended in toluene (20 ml) and stirred at 40 °C for 2.5 hours under a nitrogen atmosphere. The dark brown solution was left to cool and then filtered through alumina. The residues were washed with diethyl ether (2 x 10 ml). The combined filtrates were concentrated *in vacuo* to leave a dark red solid. This solid was recrystallised from di-*n*-butyl ether to furnish the title compound (*118*) as ruby-red prisms (0.26 g, 10%), m.p. 102-104 °C; (Found: C, 44.87; H, 2.88; N, 3.05. $C_{17}H_{13}Fe_2NO_7$ requires C, 44.88; H, 2.88; N, 3.08%); $\upsilon_{max.}$ ($CHCl_3$) 2 070 (CO), 2 035 (CO), 1 997 (CO), 1 990 (CO), and 1 597 cm^{-1} (C=C); δ_H (400 MHz, $CDCl_3$) 1.54 (3H, dd, *J* 1.5 and 6.7 Hz, =CH-C$\underline{H}_3$), 3.77 (3H, s, -OC$\underline{H}_3$), 3.98 (2H, s, -C$\underline{H}_2$-), 4.79 (1H, dq, *J* 13.5 and 6.7 Hz, =C$\underline{H}$-CH_3), 5.83 (1H, dq, *J* 13.5 and 1.5 Hz, N-C$\underline{H}$=CH-), 6.92 (1H, dd, *J* 2.4 and 8.8 Hz, $\underline{H}^1$), 7.26 (1H, d, *J* 2.4 Hz, $\underline{H}^3$), and 7.53 (1H, d, *J* 8.8 Hz, $\underline{H}^2$); *m/z* (FAB) 455 (M^+, 19%), 427 (M^+-CO, 24%), 399 (M^+-2CO, 100%), 371 (M^+-3CO, 78%), 343 (M^+-4CO, 63%), 315 (M^+-5CO, 35%) and 287 (M^+-6CO, 39%).

***N*-(2,6-Difluorobenzylidene)-2-propen-1-amine (*128*).-**

2,6-Difluorobenzaldehyde (0.51 g, 3.6 mmol) was mixed with diethyl ether (5 ml) and stirred in an ice-water cooling bath. Allylamine (0.21 g, 3.8 mmol) was added dropwise over 2 minutes. The resulting solution was stirred in the cooling bath for 0.5 hours and then at room temperature for 3 hours. The brown reaction mixture was diluted with diethyl ether (5 ml), dried over sodium carbonate, filtered and then concentrated *in vacuo* to leave an orange liquid. This liquid was distilled *in vacuo* to furnish the title compound (*128*) as a clear, colourless liquid (0.51 g, 78% yield), b.p. 56-58 °C; 0.2 mm Hg; $C_{10}H_9F_2N$ requires 181.0701, found (M^+) 181.0708; $\upsilon_{max.}$ ($CHCl_3$) 1 650 (C=N), 1 625 (C=C), and 1 240 cm^{-1} (C-F); δ_H (220 MHz, $CDCl_3$), 4.33 (2H, d, *J* 5 Hz, =N-C$\underline{H}_2$-), 5.31 (1H, dd, J_{gem} 2 Hz, J_{cis} 12 Hz) and 5.34 (1H, dd, J_{gem} 2 Hz, J_{trans} 19 Hz) (-CH=C$\underline{H}_2$), 6.10 (1H, m, -C$\underline{H}$=CH_2), 6.95 (2H, m, -$\underline{Ar}$), 7.35 (1H, m, -$\underline{Ar}$), and 8.53 (1H, s, -N=C$\underline{H}$-Ar);

m/z (C.I.) 182 (M+1, 100%).

N-(2,4,6-Trimethylbenzylidene)-2-propen-1-amine (*129*).-

2,4,6-Trimethylbenzaldehyde (2.04 g, 13.8 mmol) was diluted with diethyl ether (10 ml) and stirred in an ice-water cooling bath. Allylamine (0.79 g, 14.0 mmol) was added portionwise over 10 minutes. The reaction mixture was stirred in the ice-bath for 0.5 hours and then at room temperature for 3.25 hours. The resulting pale yellow solution was diluted with diethyl ether (10 ml), dried over sodium carbonate, filtered, and concentrated *in vacuo* to leave a pale yellow liquid. This liquid was distilled *in vacuo* to furnish the title compound (*129*) as a clear, colourless liquid (2.01 g, 81%), b.p. 118 °C; 0.2 mm Hg; $C_{13}H_{17}N$ requires 187.1357, found (M^+) 187.1351; $\upsilon_{max.}$ ($CHCl_3$) 1 650 (C=N), and 1 610 cm^{-1} (C=C); δ_H (220 MHz; $CDCl_3$) 2.22 (3H, s, -C<u>H</u>$_3$), 2.38 (3H, s, -C<u>H</u>$_3$), 2.51 (3H, s, -C<u>H</u>$_3$), 4.24 (2H, d, *J* 5 Hz, -N-C<u>H</u>$_2$-), 5.19 (1H, dd, J_{gem} 2 Hz, J_{cis} 12 Hz) and 5.23 (1H, dd, J_{gem} 2 Hz, J_{trans} 19 Hz) (-CH=C<u>H</u>$_2$), 6.10 (1H, m, -C<u>H</u>=CH$_2$), 6.84 (2H, s, -<u>Ar</u>), and 8.58 (1H, s, -N=C<u>H</u>-Ph); *m/z* (E.I.) 187 (M^+, 52%), and 147 (M^+-CH_2-CH=CH_2, 100%).

1-(Prop-2-ene)-4-phenyl-1-azabuta-1,3-diene (*131*).-

Allylamine (2.05 g, 35.9 mmol) was stirred in an ice-water cooling bath and cinnamaldehyde (*25*) (4.72 g, 35.7 mmol) added dropwise over 10 minutes. The resulting solution was stirred in the ice bath for 0.5 hours and then diluted with diethyl ether (20 ml). The ethereal solution was dried over magnesium sulphate, filtered, and concentrated *in vacuo* to furnish an orange liquid. The orange liquid was distilled *in vacuo* to give the title compound *(131)* as a clear, colourless liquid (5.08 g, 83%), b.p. 116 °C; 0.2 mm Hg; $C_{12}H_{13}N$ requires 171.1045, found (M^+) 171.1049; $\upsilon_{max.}$ ($CHCl_3$) 1 640 (C=N), 1 605 (C=C), and 1 590 cm^{-1} (C=C); δ_H (220 MHz, $CDCl_3$) 4.15 (2H, d, *J* 6 Hz, N-C<u>H</u>$_2$-CH=),

5.18 (1H, dd, J_{gem} 2 Hz, J_{cis} 12 Hz) and 5.21 (1H, dd, J_{gem} 2 Hz, J_{trans} 17 Hz) ($\underline{H}_2C$=CH-CH_2-), 6.07 (1H, m, H_2C=C$\underline{H}$-CH_2-), 6.98 (2H, m, Ph-C$\underline{H}$=C$\underline{H}$-), 7.35-7.55 (5H, m, $\underline{Ph}$), and 8.02 (1H, d, *J* 6 Hz, -N=C$\underline{H}$-CH=); *m/z* (E.I.) 171 (M^+, 37%), and 170 (M^+-1, 100%).

1-Phenyl-4-azaheptatriene (*130*).-

1-(Prop-2-ene)-4-phenyl-1-azabuta-1,3-diene (*131*) (1.22g, 7.12 mmol) was dissolved in THF (dry, 10 ml) and stirred in an ice-water cooling bath. A suspension of potassium *t*-butoxide (0.87 g, 7.12 mmol) in THF (dry, 5 ml) was added to the imine solution in one portion. The reaction mixture was stirred for 2 minutes, during which time the reaction changed colour from purple to brown, and then quenched with water (distilled, 10 ml). The yellow reaction mixture was then extracted with ethyl acetate (3 x 15 ml), and the combined organic extracts dried over magnesium sulphate, filtered, and then concentrated *in vacuo* to leave a dark brown liquid. This liquid was distilled *in vacuo* to furnish the title compound (*130*) as a clear, colourless liquid (0.17 g, 14%) a 2:1 mixture of Z_{cc}- and E_{cc}-isomers, b.p. 124 °C; 0.3 mm Hg; $C_{12}H_{13}N$ requires 171.1045, found (M^+) 171.1056; $\upsilon_{max.}$ ($CHCl_3$) 1 636 (C=N), 1 616 (C=C), and 1 577 cm^{-1} (C=C); δ_H (220 MHz, $CDCl_3$) E_{cc}-isomer: 1.84 (3H, d, *J* 7 Hz, -C$\underline{H}_3$), 6.15 (1H, dq, *J* 7 and 17 Hz, -CH=C$\underline{H}$-CH_3), 6.75 (1H, d, *J* 17 Hz, N-C$\underline{H}$=CH-CH_3), 7.07 (2H, m, Ph-C$\underline{H}$=C$\underline{H}$-), 7.35-7.65 (5H, broad m, $\underline{Ph}$-), and 8.05 (1H, d, *J* 6 Hz, -N=C$\underline{H}$-); Z_{cc}-isomer: 2.05 (3H, d, *J* 7 Hz, -C$\underline{H}_3$), 5.50 (1H, dq, *J* 7 and 12Hz, -CH=C$\underline{H}$-CH_3), 6.75 (1H, d, *J* 12 Hz, N-C$\underline{H}$=CH-CH_3), 7.07 (2H, m, Ph-C$\underline{H}$=C$\underline{H}$-), 7.35-7.65 (5H, broad m, $\underline{Ph}$-), and 8.05 (1H, d, *J* 6 Hz, -N=C$\underline{H}$-); *m/z* (E.I.) 171 (M^+, 59%), and 170(M^+-1, 100%).

1-Prop-1-ene-(4-phenyl-1-azabuta-1,3-diene)tricarbonyliron(0) (*132*).-

1-Phenyl-4-azaheptatriene (*130*) (0.17 g, 0.98 mmol) and di-iron enneacarbonyl (*17*) (0.71 g, 1.96 mmol) were suspended in diethyl ether (dry, 15 ml) and stirred at reflux under a nitrogen atmosphere for 18 hours. The brown reaction mixture was allowed to cool, 1-Phenyl-4-azaheptatriene (*130*) (0.17 g, 0.98 mmol) and di-iron enneacarbonyl (*17*) (0.71 g, 1.96 mmol) were suspended in diethyl ether (dry, 15 ml) and stirred at reflux under a nitrogen atmosphere for 18 hours. The brown reaction mixture was allowed to cool, filtered through alumina, and concentrated *in vacuo* to leave a dark red solid. This solid was chromatographed on silica using 40-60 petroleum ether:diethyl ether (15:1) as eluent. The orange band was collected and concentrated *in vacuo* to leave the title complex (*132*) as an orange solid (0.03 g, 9%); $\upsilon_{max.}$ (*n*-hexane) 2 055 (CO), 1 998 (CO), and 1 982 cm^{-1} (CO); δ_H (220 MHz; $CDCl_3$) 1.78 (3H, d, *J* 7 Hz, -C<u>H</u>$_3$), 3.25 (1H, d, *J* 17 Hz, =C<u>H</u>-Ph), 5.55 (1H, dd, *J* 17 and 11 Hz, -C<u>H</u>=CH-Ph), 6.03 (1H, dq, *J* 7 and 17 Hz, =C<u>H</u>-CH_3), 6.75 (1H, d, *J* 17 Hz, N-C<u>H</u>=CH-CH_3), 7.25-7.35 (6H, m, <u>Ph</u>- and N-C<u>H</u>-).

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